

## Supporting Information

### Controlled Cationic Polymerization Using RAFT Agents with Selenonium Cations as Metal-Free Lewis Acids: From Homogeneous to Heterogeneous Catalysis

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#### Experimental Section

**Materials.** Isobutyl vinyl ether (IBVE, 99%, Meryer), ethyl vinyl ether (EVE, 98%, TCI), propoxyethylene (PVE, 99%, Aladdin), n-butyl vinyl ether (BVE, 98%, Amethyst), 2-chloroethyl vinyl ether (Cl-EVE, 97%, Energy Chemical), 2,3-dihydrofuran (DHF, 98%, Macklin), 4-methoxystyrene (pMOS, 98%, Leyan), cyclohexene oxide (CHO, 98%, Aladdin), HCl·Et<sub>2</sub>O (2M, Infinity Scientific (Beijing) Co. Ltd.), sodium diethyldithiocarbamate trihydrate (AR, Shanghai D&B Biological Science and Technology Co.Ltd.) sodium borohydride (NaBH<sub>4</sub>, 99%, Qiangsheng), copper sulfate pentahydrate (CuSO<sub>4</sub>·5H<sub>2</sub>O, 99%, Aladdin), phenylboronic acid (97%, Macklin), 1,10-phenanthroline (1,10-Phe, 99%, Meryer), silver hexafluoroantimonate (AgSbF<sub>6</sub>, 98%, J&K), silver hexafluorophosphate (AgPF<sub>6</sub>, 98%, Aladdin), silver tetrafluoroborate (AgBF<sub>4</sub>, 97%, Energy Chemical), iodomethane (MeI, 99%, Energy Chemical), phenyl sulfide (DPHS, 98%, Aladdin), diphenyliodonium hexafluorophosphate (Ph<sub>2</sub>I<sup>+</sup>PF<sub>6</sub><sup>-</sup>, 98%, Aladdin), 4-vinylphenylboronic acid (98%, Energy Chemical), cupric sulfate (CuSO<sub>4</sub>, 98%, Energy Chemical), 2,2'-Azobis(2-methylpropionitrile) (AIBN, 98%, Aladdin), sodium carbonate (Na<sub>2</sub>CO<sub>3</sub>, 99%, Qiangsheng), ethanol (EtOH, 99%, Qiangsheng), tetrahydrofuran (THF, 99%, Qiangsheng), dichloromethane (DCM, 99%, Qiangsheng), toluene (99%, Qiangsheng), ethyl acetate (EA, 99%, Qiangsheng), n-hexane(99%, Qiangsheng), acetonitrile (99%, Qiangsheng), ethyl ether (99%, Qiangsheng), acetone (99%, Qiangsheng) and methanol (99%, Qiangsheng) were used as received without further purification. Styrene (St, 99%, Qiangsheng), vinyl acetate (VAc, 99%, Qiangsheng) and divinylbenzene (DVB, 80%, Aladdin) was purified by passing through a neutral alumina column to remove the inhibitor. The purified IBVE for comparison is prepared by distillation of IBVE from CaH<sub>2</sub>. Diphenyl diselenide (DPDSe) was synthesized according to the corresponding references<sup>1</sup>.

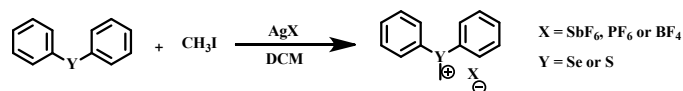
**Instrument.** The number-average molecular weights ( $M_n$ ) and molecular weight distributions ( $\mathcal{D}$ ) of polymers were measured by TOSOH HLC-8320 Size Exclusion Chromatography (SEC) equipped with refractive index and UV detectors using two TSKgel SuperMultiporeHZ-N ( $4.6 \times 150$  mm) columns arranged in series. Tetrahydrofuran (THF) was served as the eluent with a flow rate of  $0.35 \text{ mL min}^{-1}$  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. The proton nuclear magnetic resonance ( $^1\text{H}$  NMR) spectra were measured on a Bruker 300 MHz spectrometer. The samples were dissolved with deuterated trichloromethane ( $\text{CDCl}_3$ ) or dimethyl sulfoxide- $d_6$  ( $\text{DMSO-}d_6$ ) using tetramethylsilane (TMS) as an internal standard. The UV-vis absorption spectrum was measured by Shimadzu UV-2600 UV-vis spectrophotometer at room temperature. The matrix-assisted laser desorption/ionization time of flight mass spectrometry (MALDI-TOF MS) was measured using a Bruker Daltonics Ultraflex in the positive ion and reflection mode with a 337 nm nitrogen laser. Trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene malononitrile (DCTB) was used as the matrix and sodium trifluoroacetate (NaTFA) was used as ionization agents. The concentration of polymer solution is  $10 \text{ mg mL}^{-1}$  in  $\text{CHCl}_3$ . XPS was measured on the Thermo Scientific K-Alpha+, Al  $\text{K}\alpha$  source to confirm the change of the chemical structure. Morphology of the heterogeneous catalysis was characterized by SEM using Hitachi SU8010 at 5 kV. Concentrations of KOH in the commercial monomers were characterized by Thermofisher iCAPTM Qc ICP-MS and the results were concluded in Table S6.

**Synthesis of S-1-isobutoxyethyl N,N-diethyl dithiocarbamate (CTA).** The IBVE-HCl adduct was prepared by adding IBVE (8.01 g, 80 mmol) dropwise into the 2 M  $\text{Et}_2\text{O}$  solution of hydrogen chloride (40 mL, 80 mmol) at  $0$  °C, and reacting for 1 hour. Sodium diethyldithiocarbamate trihydrate (15.07 g, 88 mmol) was dissolved in 250 mL acetone by stirring in a 500 mL single-necked bottle. Then the  $\text{Et}_2\text{O}$  solution of IBVE-HCl adduct was added dropwise and the solution was stirred at room temperature for 6 hours. The resulting pale yellow solution was evaporated to remove the solvent and then washed with 5wt%  $\text{NaHCO}_3$  aqueous solution, brine and water and extracted with ethyl acetate. The organic phase was dried with  $\text{Na}_2\text{SO}_4$  and purified by column chromatography to give pure product as a pale yellow oil; yield: 11.82 g (59.2%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz; Figure S19):  $\delta$  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).

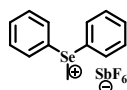
**Synthesis of diphenyl selenide (DPhSe).** In a 250 mL round bottom flask, diphenyl diselenide (4.00 g, 50 mmol) and sodium borohydride (1.90 g, 50 mmol) were added in ethanol (150 mL). Reaction solution was stirred at room temperature for 1 h under argon atmosphere. Then,  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  (1.25 g, 5 mmol), 1,10-phenanthroline (0.90 g, 1 mmol), and phenylboronic acid (6.05 g, 50 mmol) were added to the reaction solution sequentially. Reaction solution was stirred under oxygen balloon for 10 h. Then, reaction solution was poured into water and extracted with ethyl acetate. Combined organic layer was dried over  $\text{Na}_2\text{SO}_4$ , evaporated under reduced pressure

at 40 °C. The crude product was purified by column chromatography (hexane) to provide diphenyl selenide as a yellow liquid; yield: 9.80 g (84%). <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 300 MHz; Figure S20): δ 7.33 (m, 4 H), 7.43 (m, 6 H).

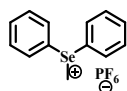
### General procedure for the synthesis of onium salts.



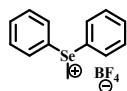
The method to prepare onium salts Se-1, Se-2, Se3, S-1 and S-2 is similar to that reported in the literature.<sup>2</sup> AgX (2.0 mmol) and the corresponding chalcogenide (2.0 mmol) were dissolved and stirred in acetonitrile (6 mL) under argon atmosphere. Then methyl iodide (4.0 mmol) was added via syringe to the stirred solution and stirred overnight in the dark at room temperature. The mixture was filtered to remove AgI, and the filtrate was evaporated under reduced pressure at 40 °C. The residue was washed with cold water and then recrystallized in ether to obtain the product.



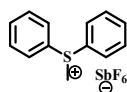
**Methyldiphenylselenonium hexafluoroantimonate (Se-1).** White solid, yield: 52%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz; Figure S21): δ 7.70-7.58 (m, 10 H), 3.40 (s, 3 H).



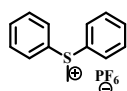
**Methyldiphenylselenonium hexafluorophosphate (Se-2).** White solid, yield: 68%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz; Figure S22): δ 7.70-7.58 (m, 10 H), 3.40 (s, 3 H).



**Methyldiphenylselenonium tetrafluoroborate (Se-3).** White solid, yield: 55%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz; Figure S23): δ 7.70-7.58 (m, 10 H), 3.44 (s, 3 H).



**Methyldiphenylsulfonium hexafluoroantimonate (S-1).** White solid, yield: 63%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz; Figure S24): δ 7.83-7.64 (m, 10 H), 3.56 (s, 3 H).



**Methyldiphenylsulfonium hexafluorophosphate (S-2).** White solid, yield: 70%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz; Figure S25): δ 7.85-7.58 (m, 10 H), 3.56 (s, 3 H).

**Synthesis of *p*-phenylselenium styrene (*p*-PhSeSt).** DPDSe (6.24 g, 20 mmol), 4-vinylphenylboric acid (6.51 g, 44 mmol), cupric sulfate (2.00 g, 30 mmol,) and 10-phenanthroline (2.30 g, 30 mmol,) were added to a 100 ml three mouth flask. EtOH (60 ml) was added to the bottle via syringe under argon atmosphere

and stirred for 10 minutes. Then Na<sub>2</sub>CO<sub>3</sub> (12 mL, 5wt% aqueous solution) was added dropwise to the reaction solution. After dropping, the mixture was strongly stirred at room temperature in air atmosphere for 22 h. Then, reaction solution was extracted with CHCl<sub>3</sub>. Combined organic layer was dried over Na<sub>2</sub>SO<sub>4</sub>, evaporated under reduced pressure at 40 °C. The crude product was purified by column chromatography (hexane) to provide *p*-phenylselenium styrene, yield: 65%. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 300 MHz; Figure S26): δ 5.27 (d, 1H), 5.82 (d, 1H), 6.67 (q, 1H), 7.34-7.44 (m, 9H).

**Homogeneous polymerization of vinyl ethers (VEs).** The polymerization of IBVE is described as a typical example. A mixture of IBVE (0.5 mL, 3.79 mmol), CTA (9.6 mg, 0.038 mmol), Se-1 (0.19 mg, 0.00038 mmol) and 0.2mL DCM was added in a 5 mL ampoule with a molar ratio of [IBVE]<sub>0</sub>:[CTA]<sub>0</sub>:[Se-1]<sub>0</sub> = 100:1:0.01. The ampoule was sealed and stirred at 25 °C. After a predetermined time, the polymerization was terminated by adding tetrahydrofuran containing methanol (1 mL solution containing 0.01 mL methanol). The polymer was dried to a constant weight in a 40 °C vacuum oven to remove unreacted IBVE and the conversion was calculated by gravimetric analysis. Then a small amount of the sample was taken for SEC testing. The polymer was diluted by THF and precipitated in methanol to obtain the purified product for further characterization.

**Heterogeneous polymerization of IBVE.** A mixture of IBVE (0.5 mL, 3.79 mmol), CTA (9.6 mg, 0.038 mmol) and heterogeneous catalysis (PS-MS-Se) (40 mg) was added in a 5 mL ampoule. The ampoule was sealed and stirred at 25 °C. After a predetermined time, the polymerization was terminated by adding tetrahydrofuran containing methanol (1 mL solution containing 0.01 mL methanol). The polymer was dried to a constant weight in a 40 °C vacuum oven to remove unreacted IBVE and the conversion was calculated by gravimetric analysis. Then a small amount of the sample was taken for SEC testing. The heterogeneous catalyst was separated by washing with THF and centrifugation. Then it was dried in a 40 °C vacuum oven for reuse.

#### **Chain extension.**

(a) A mixture of IBVE (0.5 mL, 3.79 mmol), purified PIBVE (27 mg, 0.009 mmol), Se-1 (0.04 mg, 0.00009 mmol) and 0.2mL DCM was added in a 5 mL ampoule with a molar ratio of [IBVE]<sub>0</sub>:[PIBVE]<sub>0</sub>:[Se-1]<sub>0</sub> = 400:1:0.01. The ampoule was sealed and stirred at 25 °C. After a predetermined time, the polymerization was terminated by adding tetrahydrofuran containing methanol (1 mL solution containing 0.01 mL methanol). The polymer was dried to a constant weight in a 40 °C vacuum oven to remove unreacted IBVE and the conversion was calculated by gravimetric analysis. Then a small amount of the sample was taken for SEC testing. The polymer was diluted by THF and precipitated in methanol for purification.

(b) A mixture of EVE (0.5 mL, 5.22 mmol), purified PIBVE (39 mg, 0.013 mmol), Se-1 (0.06 mg, 0.00013 mmol) and 0.2mL DCM was added in a 5 mL ampoule

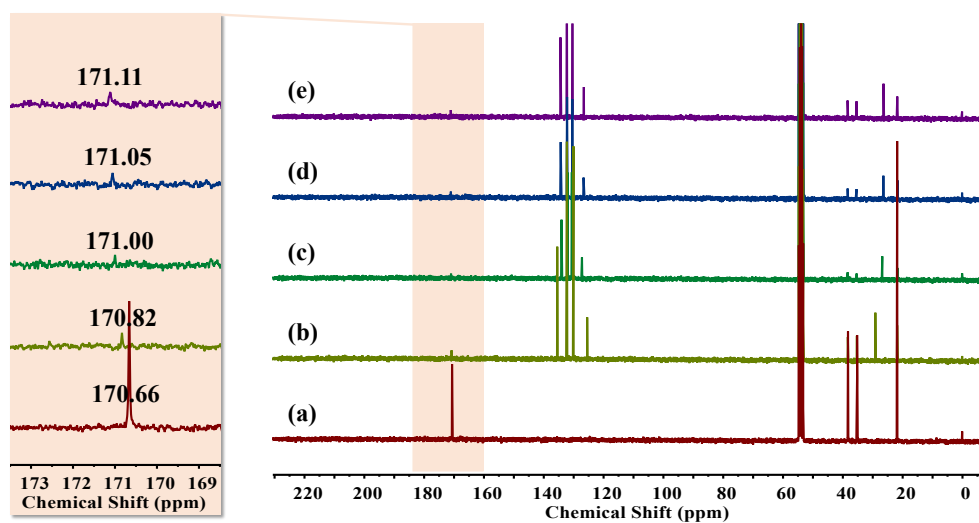
with a molar ratio of  $[EVE]_0:[PIBVE]_0:[Se-1]_0 = 400:1:0.01$ . The ampoule was sealed and stirred at 25 °C. After a predetermined time, the polymerization was terminated by adding tetrahydrofuran containing methanol (1 mL solution containing 0.01 mL methanol). The polymer was dried to a constant weight in a 40 °C vacuum oven to remove unreacted EVE and the conversion was calculated by gravimetric analysis. Then a small amount of the sample was taken for SEC testing. The polymer was diluted by THF and precipitated in methanol for purification.

(c) A mixture of VAc (0.5 mL, 5.37 mmol), purified PIBVE (40 mg, 0.013 mmol), AIBN (0.44 mg, 0.0026 mmol) and 0.1 mL toluene was added in a 5 mL ampoule with a molar ratio of  $[VAc]_0:[PIBVE]_0:[AIBN]_0 = 400:1:0.2$ . The ampoule was sealed after deaeration and stirred at 70 °C. After a predetermined time, the polymerization was terminated by adding tetrahydrofuran and exposure to air. The polymer was dried to a constant weight in a 40 °C vacuum oven to remove unreacted VAc and the conversion was calculated by gravimetric analysis. Then a small amount of the sample was taken for SEC testing. The polymer was diluted by THF and precipitated in hexane for purification.

**Preparation of polystyrene microspheres containing diphenyl monoselenide structure.** In a 250 mL Schlenk bottle, DVB (1 mL, 7.06 mmol), St (0.46 g, 4.41 mmol), p-PhSeSt (1.14 g, 4.41 mmol) and AIBN (0.04 g, 0.24 mmol) were added to 70 mL of ethanol. After mixing well, the oxygen in the reaction bottle was removed with argon. The reaction solution was slowly heated to 70 °C and reacted at constant temperature for 24 h. After the reaction, the mixture was cooled to room temperature. The mixture was filtered and then the solid obtained was washed with acetonitrile, tetrahydrofuran and acetone for several times. Then the polystyrene microspheres containing diphenyl monoselenide structure were dried to a constant weight in a 40 °C vacuum.

**Preparation of heterogeneous catalyst.** The method to prepare heterogeneous catalyst are similar to that of onium salts.  $AgSbF_6$  (2.0 mmol) and the polystyrene microspheres containing diphenyl monoselenide structure (2.0 mmol) were dissolved and stirred in acetonitrile (6 mL) under argon atmosphere. Then methyl iodide (4.0 mmol) was added via syringe to the stirred solution and stirred overnight in the dark at room temperature. The mixture was filtered to remove the solvent and washed with cold water and ether. Finally, the heterogeneous catalyst was dried in a 40 °C vacuum.

## Additional Results

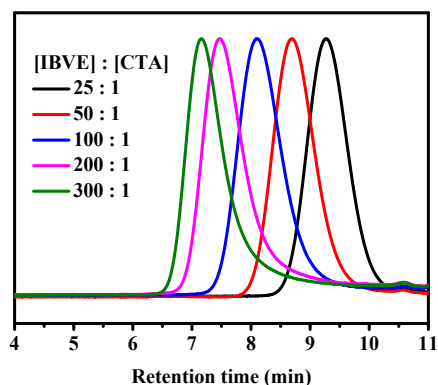


**Figure S1.** The C=O signal in DMAC in the  $^{13}\text{C}$  NMR experiments on the mixture of DMAC and onium salt (1:1) in  $\text{CD}_2\text{Cl}_2$ ; a) DMAC; b) DMAC+S-1; c) DMAC+Se-3; d) DMAC+Se-2; e) DMAC+Se-1.

**Table S1.** Polymerization of IBVE using different onium salts as Lewis acid catalyst in DCM at 25 °C,  $V_{\text{IBVE}} = 0.5$  mL,  $V_{\text{DCM}} = 0.2$  mL.

| Entry | Catalyst | $[\text{M}]_0:[\text{CTA}]_0:[\text{Catalyst}]_0$ | Time | Conv.% | <sup>a</sup> $M_{n,\text{th}}$ | <sup>b</sup> $M_{n,\text{SEC}}$ | $\bar{D}$ |
|-------|----------|---|------|--------|--------------------------------|---------------------------------|-----------|
| 1     | Se-1     | 100:0:0.01  | 24 h | -      | -                              | -                               | -         |
| 2     | Se-2     | 100:0:0.01  | 24 h | -      | -                              | -                               | -         |
| 3     | Se-3     | 100:0:0.01  | 24 h | -      | -                              | -                               | -         |
| 4     | S-1      | 100:0:0.01  | 24 h | -      | -                              | -                               | -         |
| 5     | S-2      | 100:0:0.1   | 24 h | -      | -                              | -                               | -         |
| 6     | I-1      | 100:0:0.1   | 24 h | -      | -                              | -                               | -         |
| 7     | -        | 100:1:0   | 24 h | -      | -                              | -                               | -         |

<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 SEC using PS as a standard in THF.

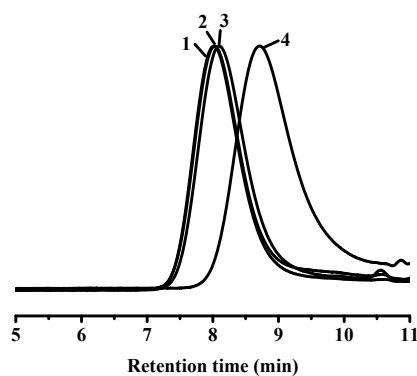


**Figure S2.** SEC traces of PIBVE obtained with the different molar ratio ( $[\text{IBVE}]_0/[\text{CTA}]_0$ ) in Table 2 Entries 5 and 7-10.

**Table S2.** Polymerization of IBVE using purified reagents in the presence of different amounts of water with the molar ratio  $[\text{IBVE}]_0:[\text{CTA}]_0:[\text{Catalyst}]_0:[\text{H}_2\text{O}]_0 = 100:1:0.01:x$  in DCM at 25 °C,  $V_{\text{IBVE}} = 0.5 \text{ mL}$ ,  $V_{\text{DCM}} = 0.2 \text{ mL}$ .

| Entry | x   | Time   | Conv.% | <sup>a</sup> $M_{n,\text{th}}$ | <sup>b</sup> $M_{n,\text{SEC}}$ | $\mathcal{D}$ |
|-------|-----|--------|--------|--------------------------------|---------------------------------|---------------|
| 1     | -   | 30 min | 96.3   | 9900                           | 10400                           | 1.13          |
| 2     | 0.1 | 30 min | 98.8   | 10100                          | 10300                           | 1.14          |
| 3     | 1.0 | 60 min | 94.4   | 9700                           | 9100                            | 1.15          |
| 4     | 1.5 | 60 min | 93.5   | 9600                           | 4600                            | 1.26          |

<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 SEC using PS as a standard in THF

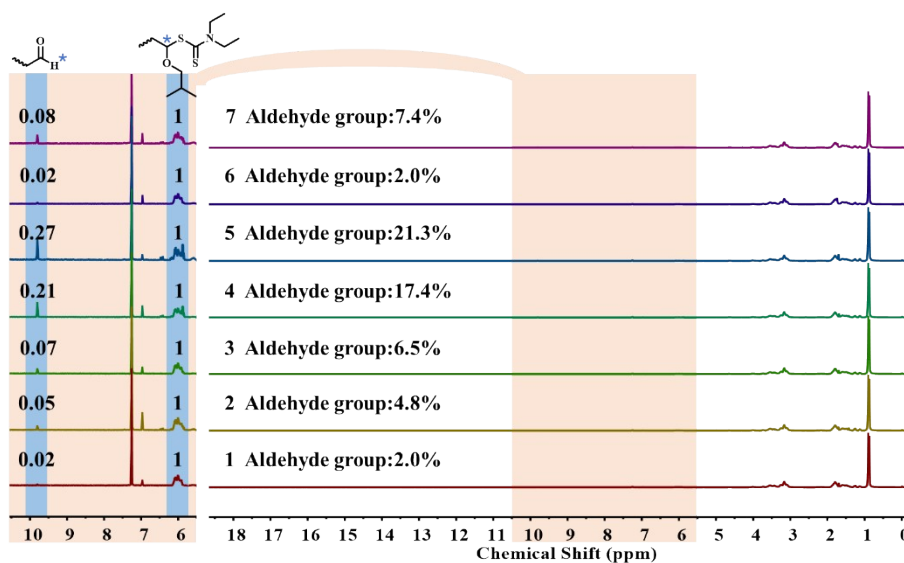


**Figure S3.** SEC traces of PIBVE obtained in Table S2.

**Table S3.** Polymerization of IBVE using purified reagents in the presence of different amounts of water with the molar ratio  $[\text{IBVE}]_0:[\text{CTA}]_0:[\text{Se-1}]_0:[\text{H}_2\text{O}]_0 = 25:1:0.001:x$  in DCM at 25 °C,  $V_{\text{IBVE}} = 0.5 \text{ mL}$ ,  $V_{\text{DCM}} = 0.2 \text{ mL}$ .

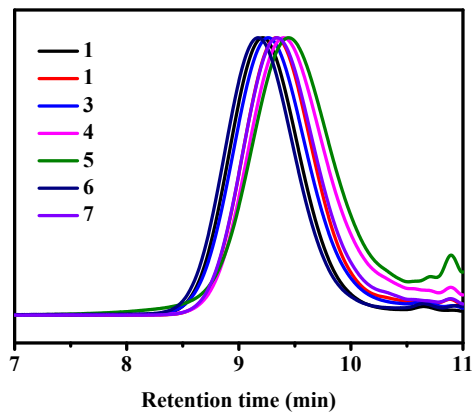
| Entry          | x   | Time    | Conv.% | <sup>a</sup> $M_{n,\text{th}}$ | <sup>b</sup> $M_{n,\text{SEC}}$ | $\bar{D}$ |
|----------------|-----|---------|--------|--------------------------------|---------------------------------|-----------|
| 1              | -   | 45 min  | 97.6   | 2700                           | 3300                            | 1.12      |
| 2              | 0.2 | 45 min  | 88.7   | 2500                           | 2900                            | 1.13      |
| 3              | 0.5 | 60 min  | 96.0   | 2700                           | 3000                            | 1.16      |
| 4              | 1.0 | 90 min  | 95.1   | 2600                           | 2600                            | 1.16      |
| 5              | 1.5 | 120 min | 88.5   | 2500                           | 2600                            | 1.16      |
| <sup>c</sup> 6 | -   | 30 min  | 99.5   | 2700                           | 3500                            | 1.12      |
| <sup>c</sup> 7 | 0.5 | 60 min  | 89.3   | 2500                           | 2800                            | 1.15      |

<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 SEC using PS as a standard in THF; <sup>c</sup> Polymerization using unpurified IBVE.

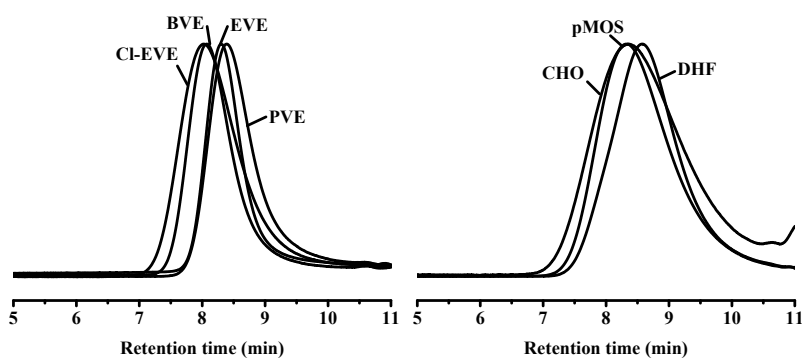


**Figure S4.** <sup>1</sup>H NMR spectra of PIBVE obtained in Table S3 in CDCl<sub>3</sub>.

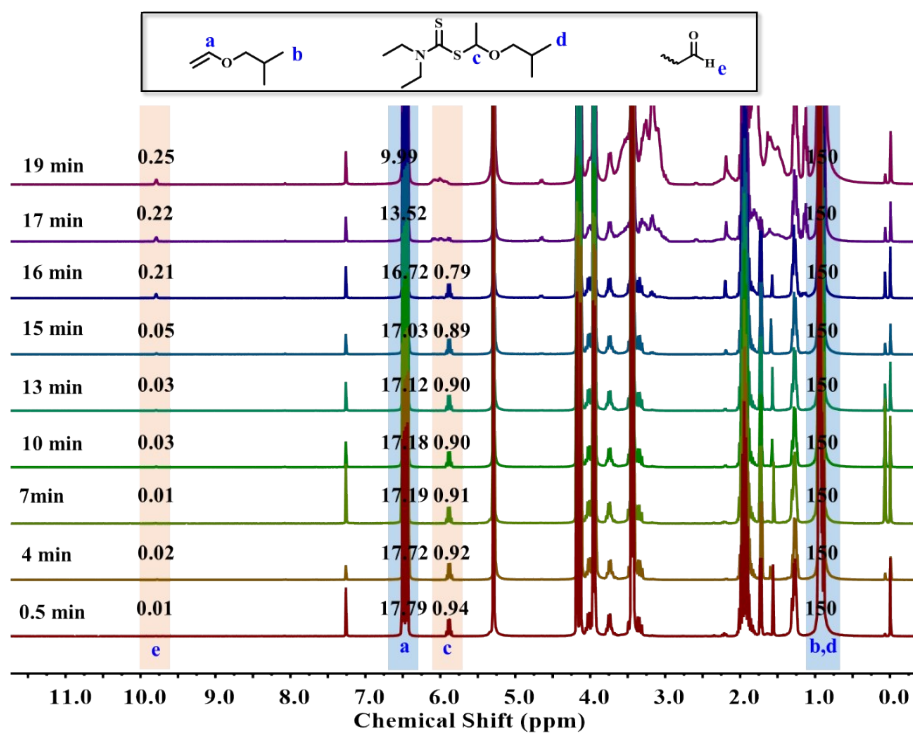




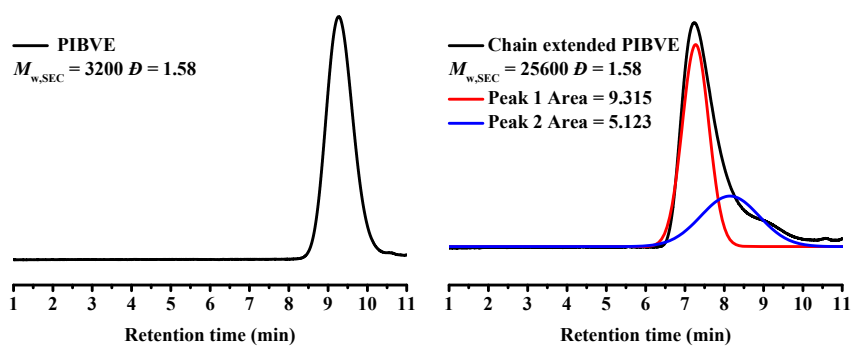
**Figure S5.** SEC traces of PIBVE obtained in Table S3.



**Figure S6.** SEC traces of polymers obtained with different monomers using Se-1 as Lewis acid in Table 3.



**Figure S7.**  $^1\text{H}$  NMR spectra of polymerization with the molar ratio  $[\text{IBVE}]_0:[\text{CTA}]_0:[\text{Se-1}]_0 = 25:1:0.001$  at  $25^\circ\text{C}$ ,  $V_{\text{IBVE}} = 0.5\text{ mL}$ ,  $V_{\text{DCM}} = 0.2\text{ mL}$  in  $\text{CDCl}_3$ .



**Figure S8.** SEC traces of PIBVE before and after chain extension and the peak splitting results of SEC traces of PIBVE after chain extension.

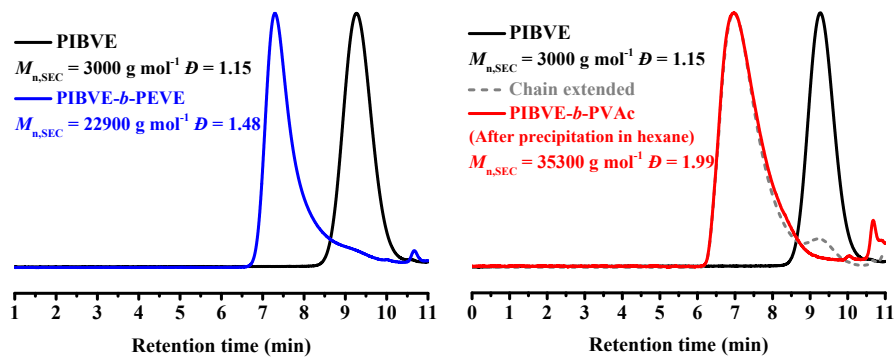


Figure S9. SEC traces of polymers obtained before and after chain extension.

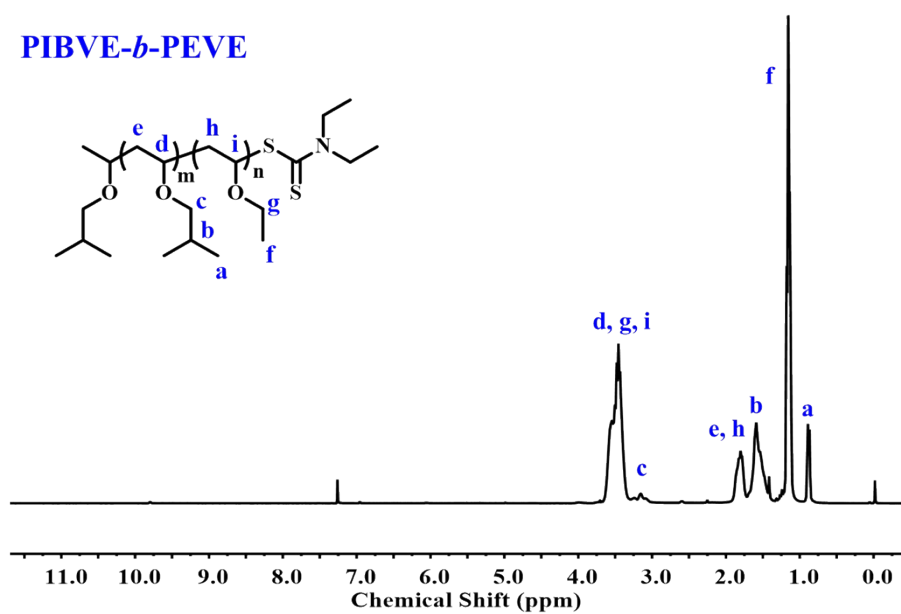
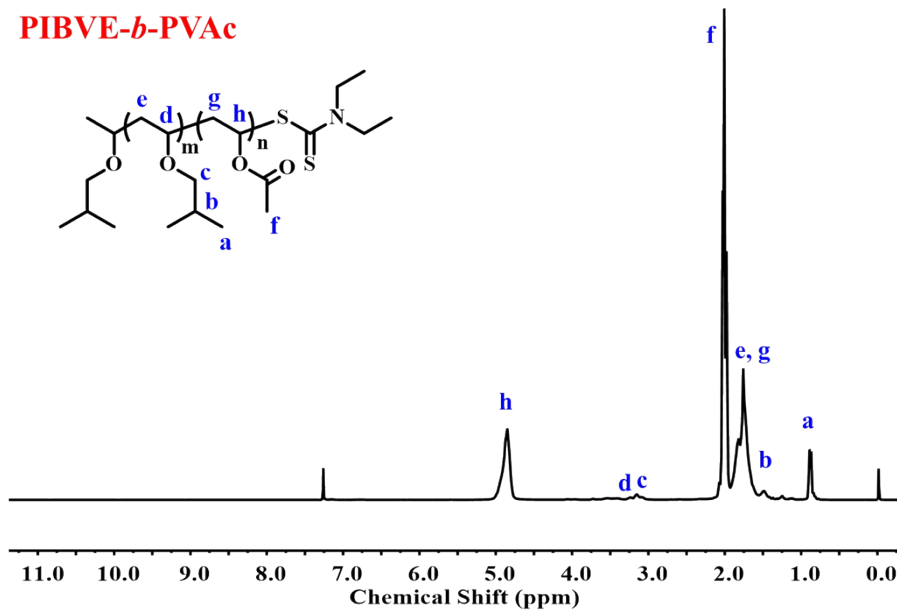
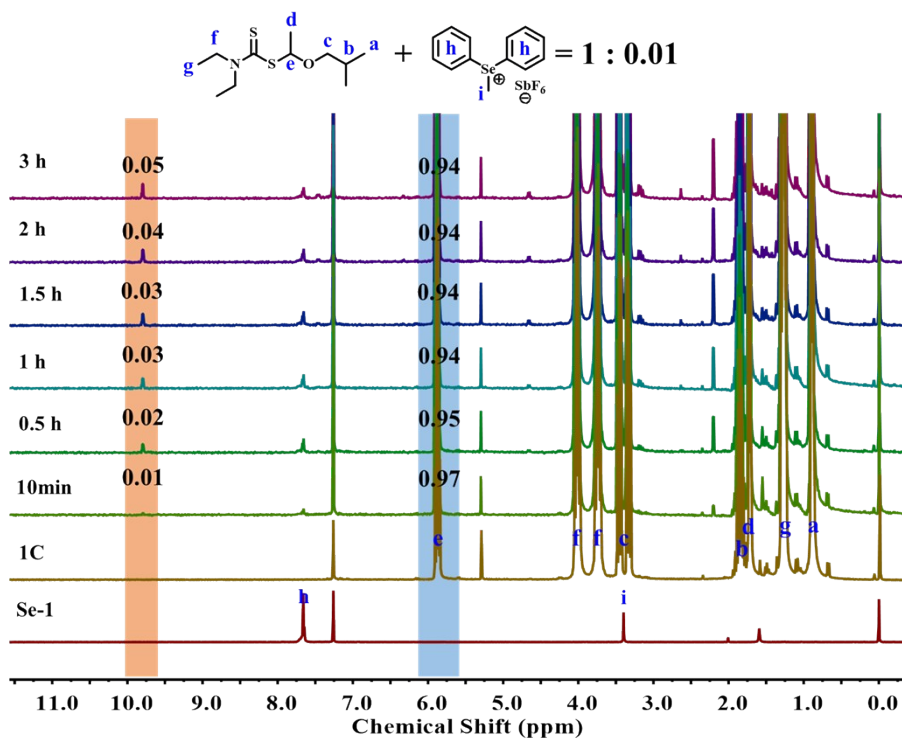


Figure S10.  $^1\text{H}$  NMR spectra of PIBVE-*b*-PEVE in  $\text{CDCl}_3$ .

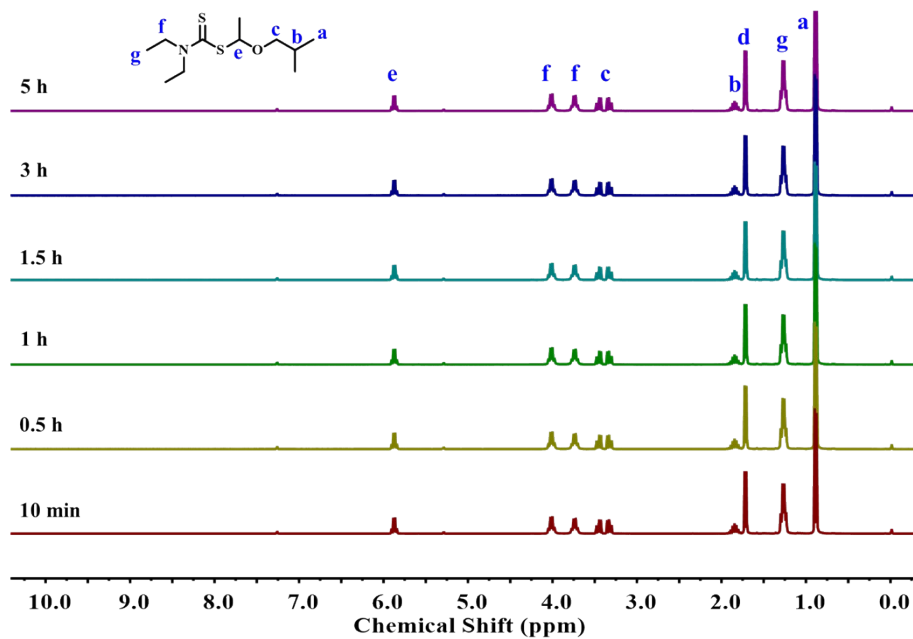
**PIBVE-*b*-PVAc**



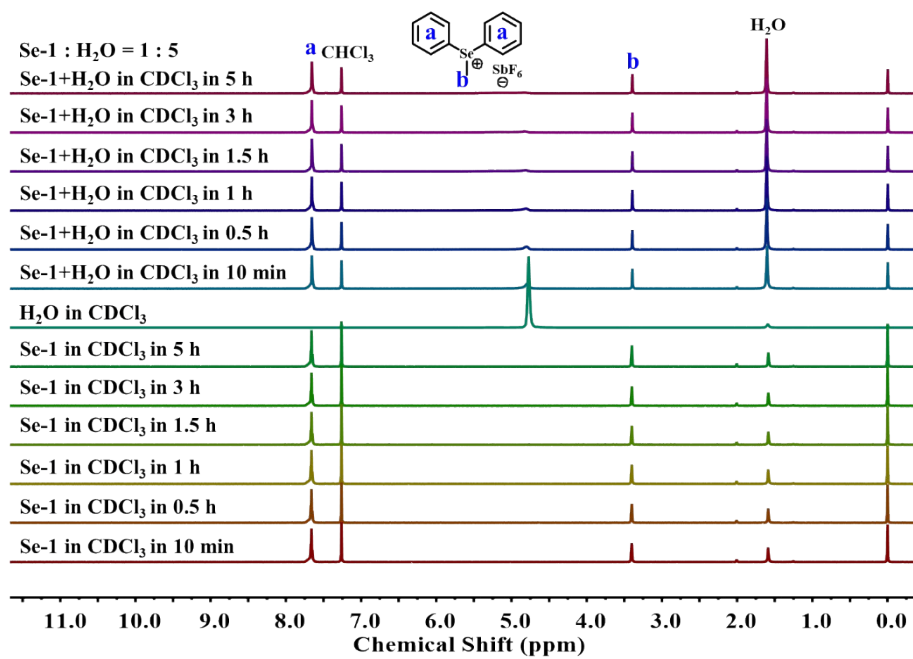
**Figure S11.** <sup>1</sup>H NMR spectra of PIBVE-*b*-PVAc in CDCl<sub>3</sub>.



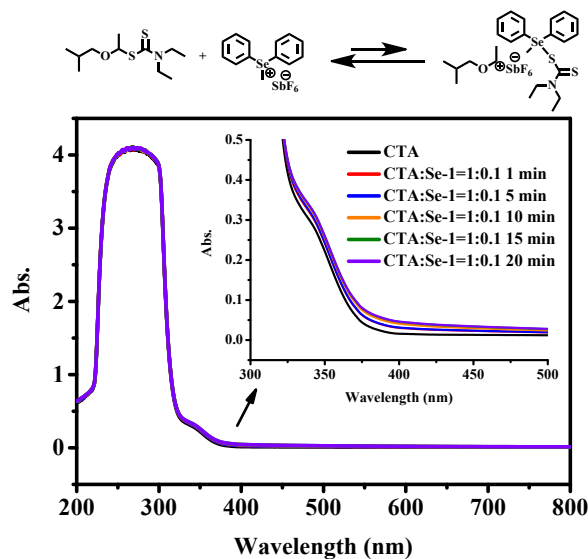
**Figure S12.** <sup>1</sup>H NMR spectra of CTA and Se-1 the molar ratio [CTA]<sub>0</sub>:[ Se-1]<sub>0</sub> = 1:0.01 in CDCl<sub>3</sub>.



**Figure S13.**  $^1\text{H}$  NMR spectra of CTA in  $\text{CDCl}_3$ .



**Figure S14.**  $^1\text{H}$  NMR spectra of Se-1 and Se-1+ $\text{H}_2\text{O}$  in  $\text{CDCl}_3$ .

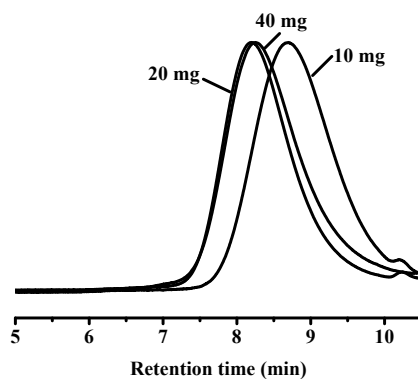


**Figure S15.** UV-vis spectra of CTA and Se-1 the molar ratio  $[CTA]_0:[Se-1]_0 = 1:0.1$  in DCM.

**Table S4.** Polymerization of IBVE with the molar ratio  $[IBVE]_0:[CTA]_0 = 100:1$  at 25 °C,  $V_{IBVE} = 0.5$  mL under different amounts of heterogeneous catalyst.

| Entry | Catalyst | Time | Conv.% | <sup>a</sup> $M_{n,th}$ | <sup>b</sup> $M_{n,SEC}$ | $\bar{D}$ |
|-------|----------|------|--------|-------------------------|--------------------------|-----------|
| 1     | 10 mg    | 21 h | 43.9   | 4600                    | 4700                     | 1.32      |
| 2     | 20 mg    | 21 h | 82.6   | 8500                    | 7900                     | 1.23      |
| 3     | 40 mg    | 21 h | 92.2   | 9500                    | 7200                     | 1.29      |

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

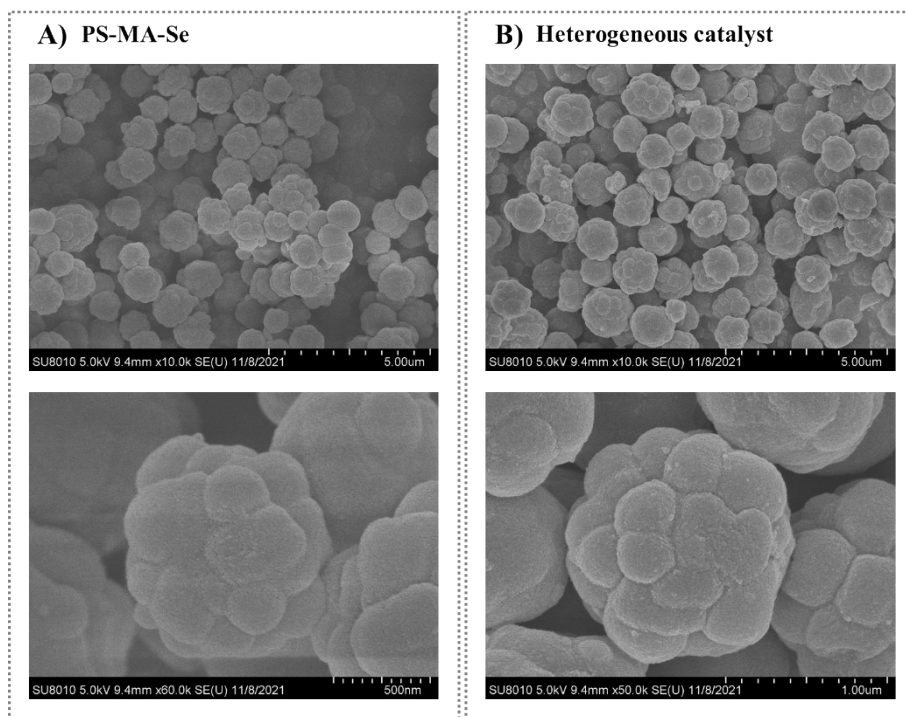


**Figure S16.** SEC traces of PIBVE under different amounts of heterogeneous catalyst in Table S4.

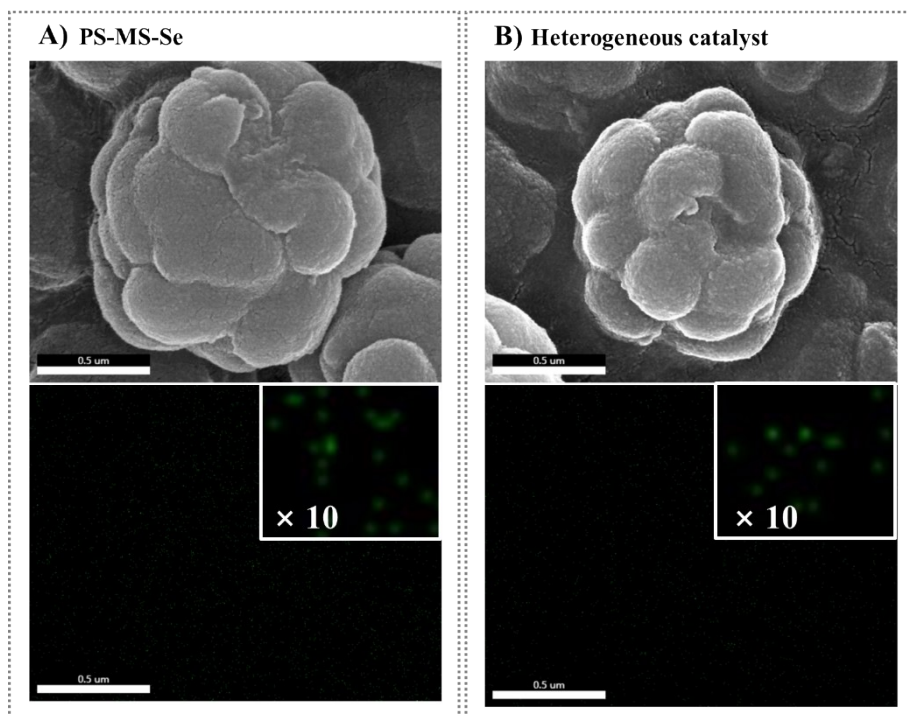
**Table S5.** Polymerization of IBVE with the molar ratio  $[\text{IBVE}]_0:[\text{CTA}]_0 = 100:1$  at 25 °C,  $V_{\text{IBVE}} = 0.5$  mL under recycled heterogeneous catalyst.

| Entry | Time | Conv.% | <sup>a</sup> $M_{n,\text{th}}$ | <sup>b</sup> $M_{n,\text{SEC}}$ | $\bar{D}$ |
|-------|------|--------|--------------------------------|---------------------------------|-----------|
| 1     | 21 h | 92.2   | 9500                           | 7200                            | 1.29      |
| 2     | 21 h | 90.1   | 9300                           | 8700                            | 1.24      |
| 3     | 21 h | 70.5   | 7300                           | 8100                            | 1.20      |
| 4     | 21 h | 62.3   | 6500                           | 6600                            | 1.24      |
| 5     | 21 h | 60.9   | 6300                           | 6700                            | 1.20      |

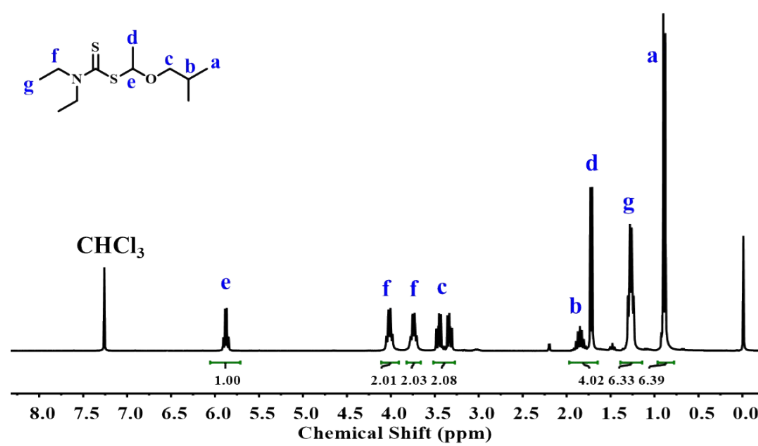
<sup>a</sup> Calculated based on conversion ( $M_{n,\text{th}} = [\text{M}]_0/[\text{CTA}]_0 \times M_{\text{IBVE}} \times \text{conversion} + M_{\text{CTA}}$ ); <sup>b</sup> determined by SEC using PS as a standard in THF.



**Figure S17.** SEM image of polystyrene microsphere containing diphenyl monoselenide (named PS-MS-Se) and heterogeneous catalyst.



**Figure S18.** SEM-EDX elemental mapping image of Se of a single microsphere.



**Figure S19.** <sup>1</sup>H NMR spectra of CTA in CDCl<sub>3</sub>.



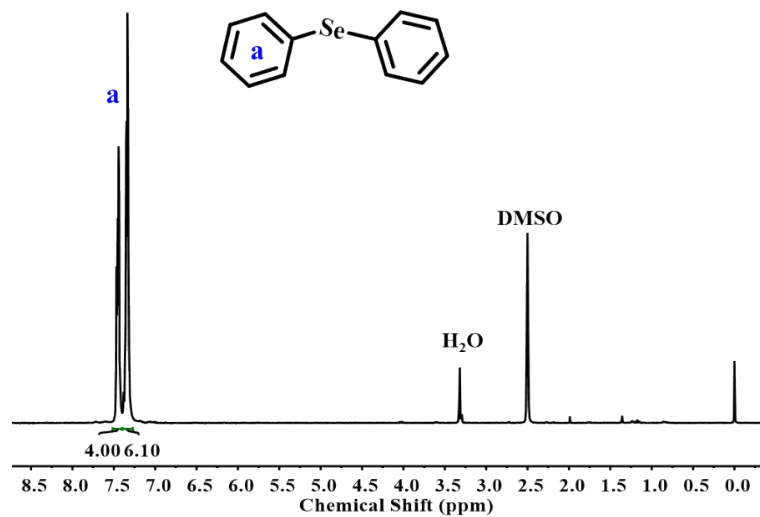


Figure S20.  $^1\text{H}$  NMR spectra of DPhSe in  $\text{CDCl}_3$ .

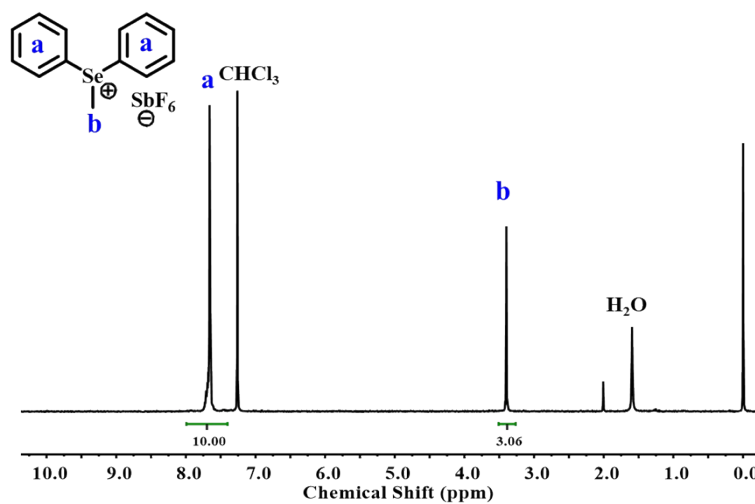


Figure S21.  $^1\text{H}$  NMR spectra of Se-1 in  $\text{CDCl}_3$ .

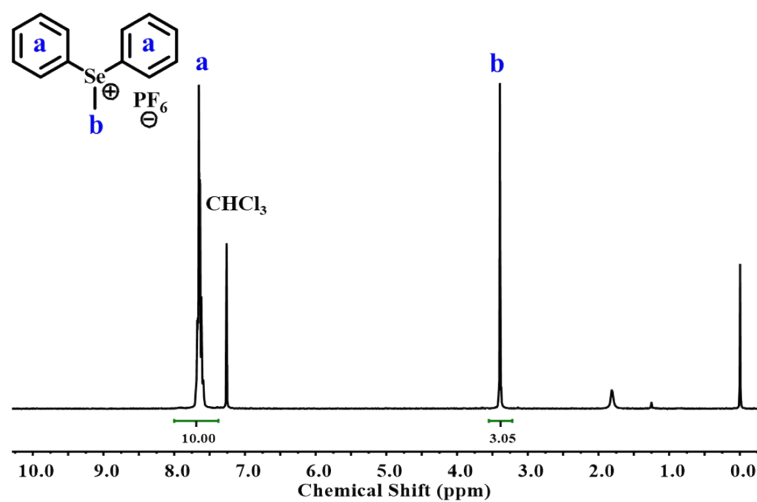


Figure S22. <sup>1</sup>H NMR spectra of Se-2 in CDCl<sub>3</sub>.

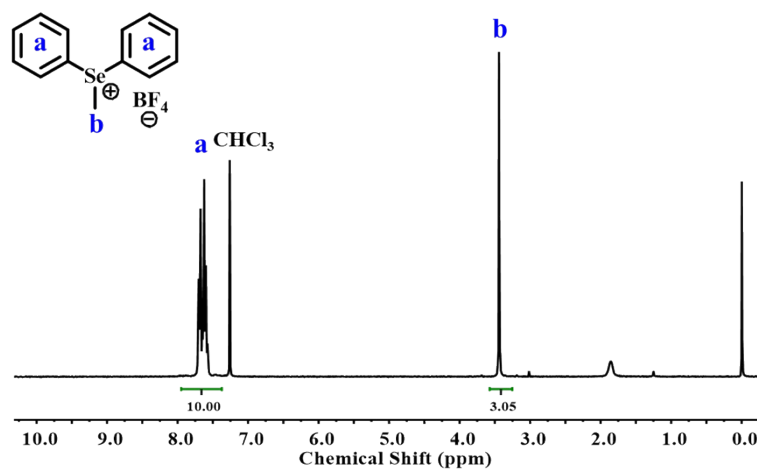


Figure S23. <sup>1</sup>H NMR spectra of Se-3 in CDCl<sub>3</sub>.

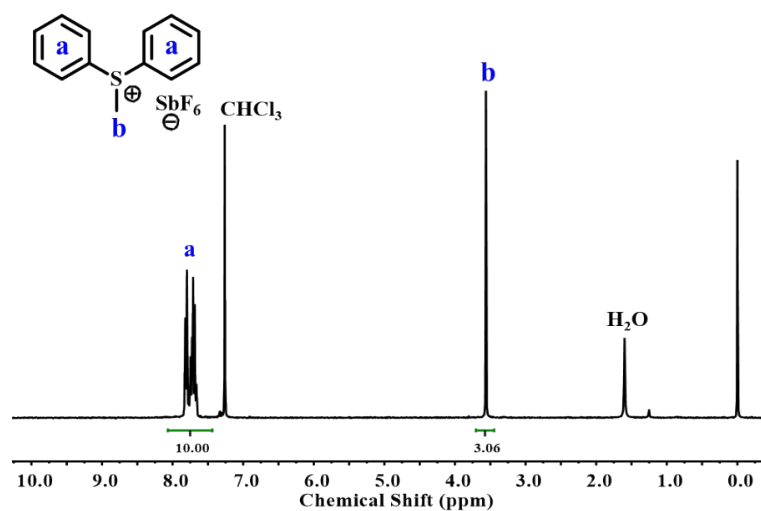


Figure S24. <sup>1</sup>H NMR spectra of S-1 in CDCl<sub>3</sub>.

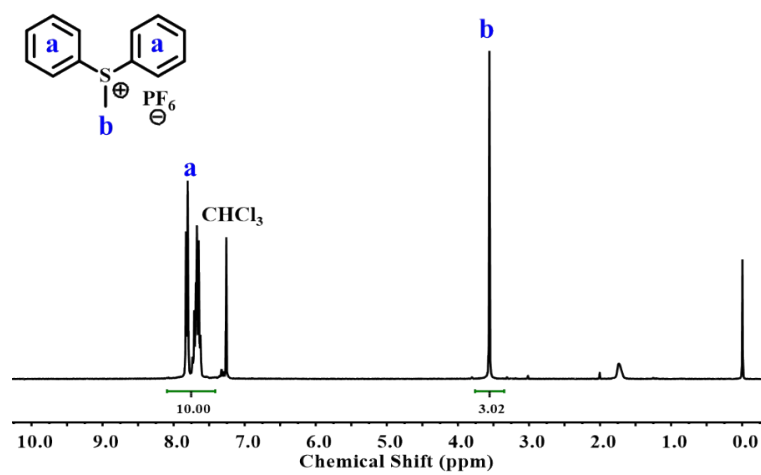
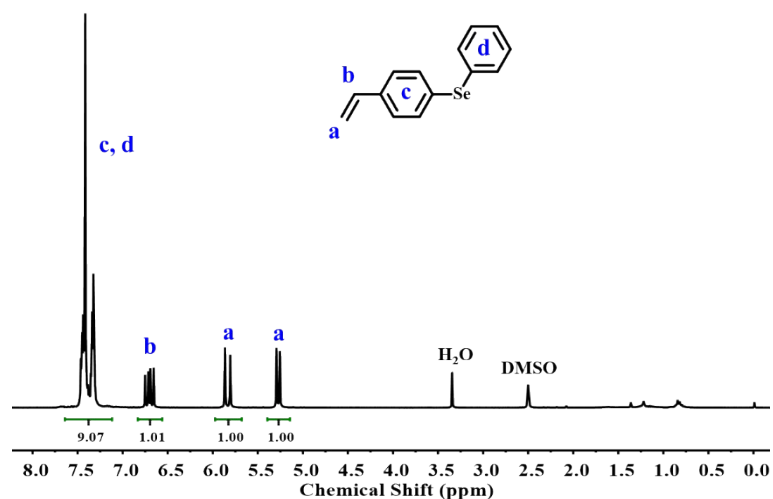


Figure S25. <sup>1</sup>H NMR spectra of S-2 in CDCl<sub>3</sub>.



**Figure S26.** <sup>1</sup>H NMR spectra of *p*-PhSeSt in DMSO-*d*<sub>6</sub>.

**Table S6.** Concentration of KOH in the commercial monomers.

| Monomer       | Concentration of KOH |
|---------------|----------------------|
| IBVE          | 0.000285%wt          |
| EVE           | 0.000115%wt          |
| PVE           | 0.000090%wt          |
| BVE           | 0.000285%wt          |
| DHF           | 0.000160%wt          |
| Cl-EVE        | 0.000175%wt          |
| <i>p</i> -MOS | 0.000055%wt          |
| CHO           | 0.000120%wt          |

Reference:

- 1 C. Ding, C. Fan, G. Jiang, J. Zhang, X. Li, N. Li, X. Pan, Z. Zhang, W. Zhang, J. Zhu, X. Zhu, *Polym. Chem.* **2015**, *6*, 6416–6423.
- 2 X. He, X. Wang, Y. S. Tse, Z. Ke, Y. Y. Yeung, *Angew. Chem. Int. Ed.* **2018**, *57*, 12869–12873.