Supporting Information

Living cationic polymerization of vinyl ethers initiated by electrophilic selenium reagents under ambient conditions

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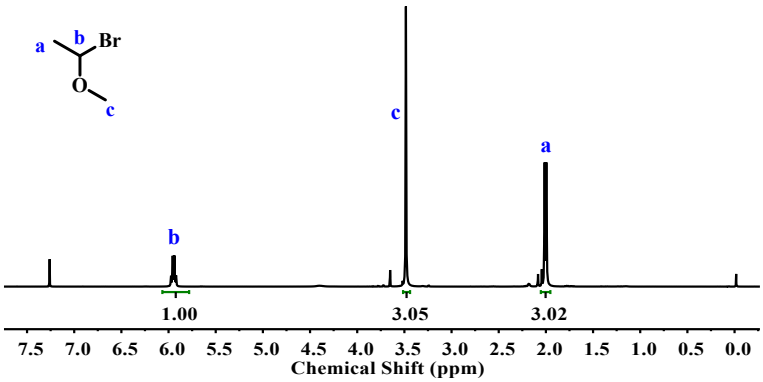


Figure S1. ^{1}H NMR spectra of bromoethyl methylether in $CDCl_3$.

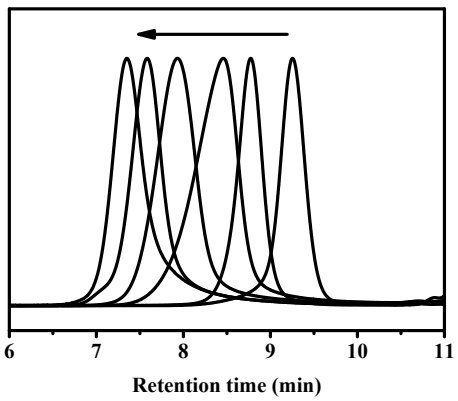


Figure S2.SEC traces versus conversion of bulk polymerization of IBVE with the diferent molar ratio ($[IBVE]_0/[PhSeBr]_0$) entries 1-6 in Table 1.

Table S1. Polymerization of IBVE with the molar ratio $[IBVE]_0 : [PhSeBr]_0 : [Mn(CO)_5Br]_0 = 100 : 1 : 0.1$ under various solvents at 25 °C, $V_{IBVE} = V_{solvent} = 0.5$ mL.

Entry	Solvent	Time	Conv.%	[a] $M_{n,th}$ (g mol^{-1})	[b] $M_{n,SEC}$ (g mol^{-1})	$Đ$
1	Toluene	7 h	95.5	9800	12600	1.15
2	EA	7 h	69.8	7200	5300	1.42
3	Hexane	7 h	97.6	10000	13100	1.09

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

Table S2. Bulk polymerization of IBVE with the molar ratio $[IBVE]_0 : [PhSeBr]_0 : [Catalyst]_0 = 200 : 1 : 0.1$ under various Lewis acid catalysts at 25 °C in glove box.

Entry	Catalyst	Time	Conv.%	[a] $M_{n,th}$ (g mol^{-1})	[b] $M_{n,SEC}$ (g mol^{-1})	$Đ$
1	$ZnCl_2$	0.08 h	95.6	19400	20200	1.26
2	$AlCl_3$	0.33 h	78.3	15900	25600	2.16
3	$TiCl_4$	0.33 h	88.7	18000	13600	1.29

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

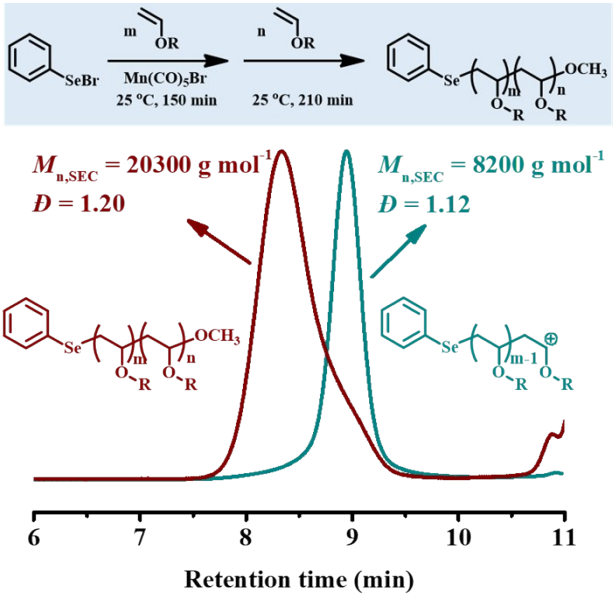


Figure S3. *In-situ* chain extension via cationic polymerization initiated with PhSeBr.

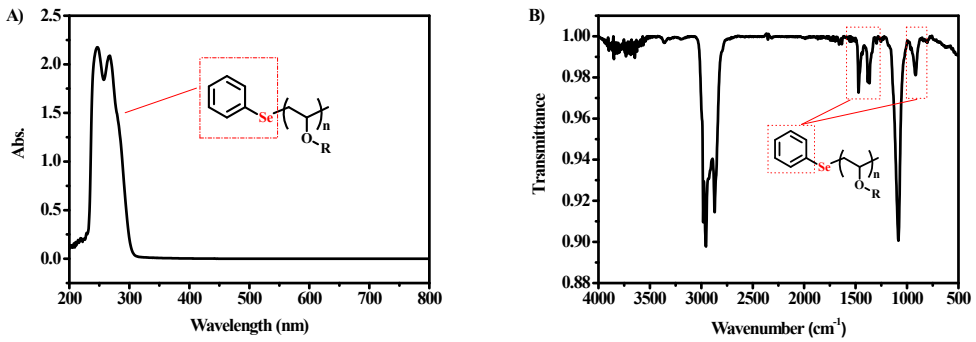


Figure S4. A) UV-*vis* absorption of PIBVE in THF; B) FT-IR spectrum of PIBVE ($M_{n,SEC}$ = 6600 g mol^{-1}, $Đ$ = 1.08).

Table S3. Bulk polymerization of IBVE under various conditions at 25 °C.

Entry	$[M]_0$: $[PhSeBr]_0$: $[Mn(CO)_5Br]_0$	Time	Conv.%	[a] $M_{n,th}$ (g mol^{-1})	[b] $M_{n,SEC}$ (g mol^{-1})	$Đ$
1	200 : 1 : 1	0.5 h	70.1	14200	17400	1.11
2	200 : 1 : 0.2	1 h	60.1	12500	13500	1.10
3	200 : 1 : 0.05	3 h	90.0	18200	21800	1.08
4	200 : 1 : 0.02	5 h	82.7	16700	17400	1.09
5	200 : 1 : 0.01	21 h	75.5	15100	22100	1.09
6	200 : 1 : 0.005	31 h	65.9	13200	15700	1.11

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

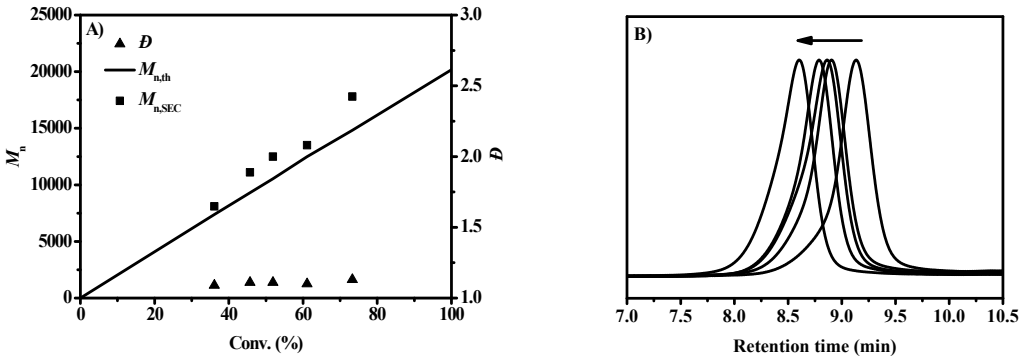


Figure S5. Bulk polymerization results of IBVE with the molar ratio $[IBVE]_0$: $[PhSeBr]_0$: $[Mn(CO)_5Br]_0$ = 200 : 1 : 0.2 at 25 °C. A) molecular weight (M_n) and molecular weight distribution ($Đ$) versus conversion; B) SEC traces.

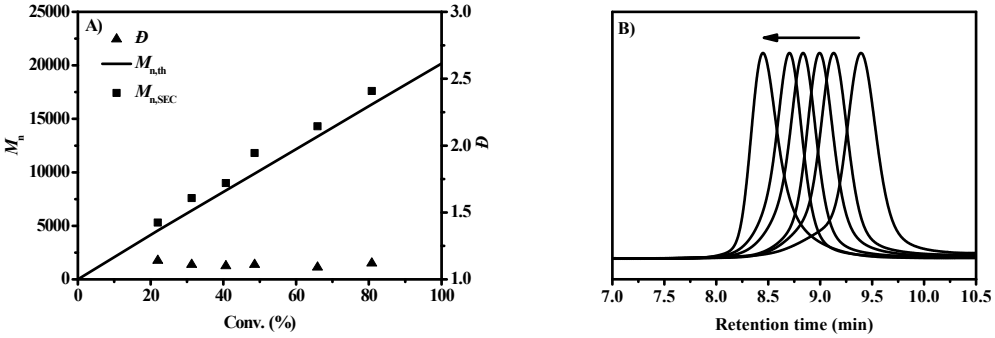


Figure S6. Bulk polymerization results of IBVE with the molar ratio $[IBVE]_0$: $[PhSeBr]_0$: $[Mn(CO)5Br]_0$ = 200 : 1 : 0.05 at 25 °C. A) molecular weight (*M*n) and molecular weight distribution (*Đ*) versus conversion; B) SEC traces.

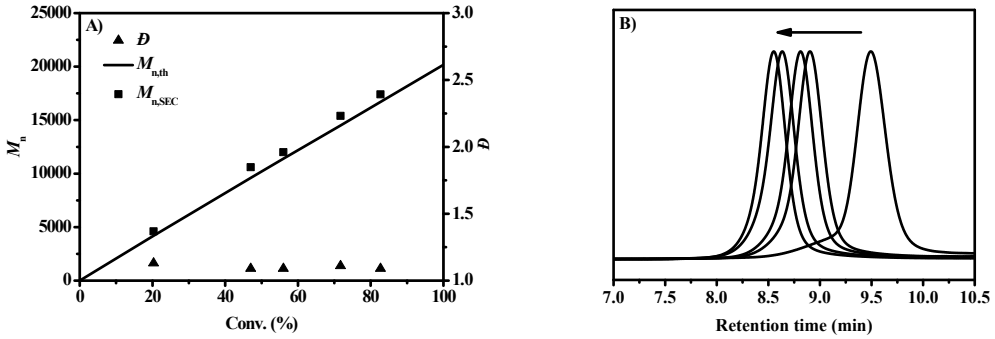


Figure S7. Bulk polymerization results of IBVE with the molar ratio $[IBVE]_0$: $[PhSeBr]_0$: $[Mn(CO)_5Br]_0$ = 200 : 1 : 0.02 at 25 °C. A) molecular weight (M_n) and molecular weight distribution (*Đ*) versus conversion; B) SEC traces.

Table S4. Bulk polymerization of IBVE with BnSeBr as initiator at 25 °C.

Entry	$[IBVE]_0$: $[BnSeBr]_0$: $[Mn(CO)_5Br]_0$	Time	Conv.%	[a] $M_{n,th}$ (g mol^{-1})	[b] $M_{n,SEC}$ (g mol^{-1})	*Đ*
1	50 : 1 : 0.1	2.5 h	52.3	2800	7800	1.12
2	100 : 1 : 0.1	3 h	98.3	10000	25400	1.16
3	200 : 1 : 0.2	3 h	95.5	13900	33400	1.28
4	100 : 1 : 0	24 h	-	-	-	-

[a] Calculated based on conversion ($M_{n,th}$ = $[M]_0/[BnSeBr]_0$ × conversion × *M* + M_{BnSeBr}).
[b] Determined by SEC using polystyrene (PS) as standard in tetrahydrofuran (THF).

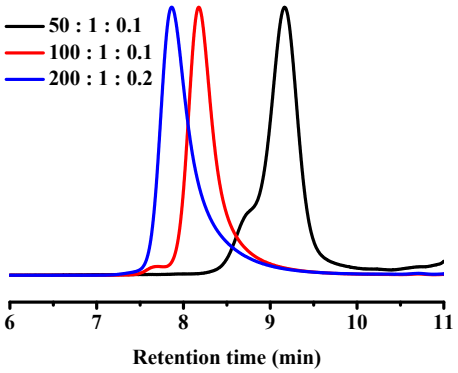


Figure S8. SEC traces of PIBVE with BnSeBr as initiator under various rates.

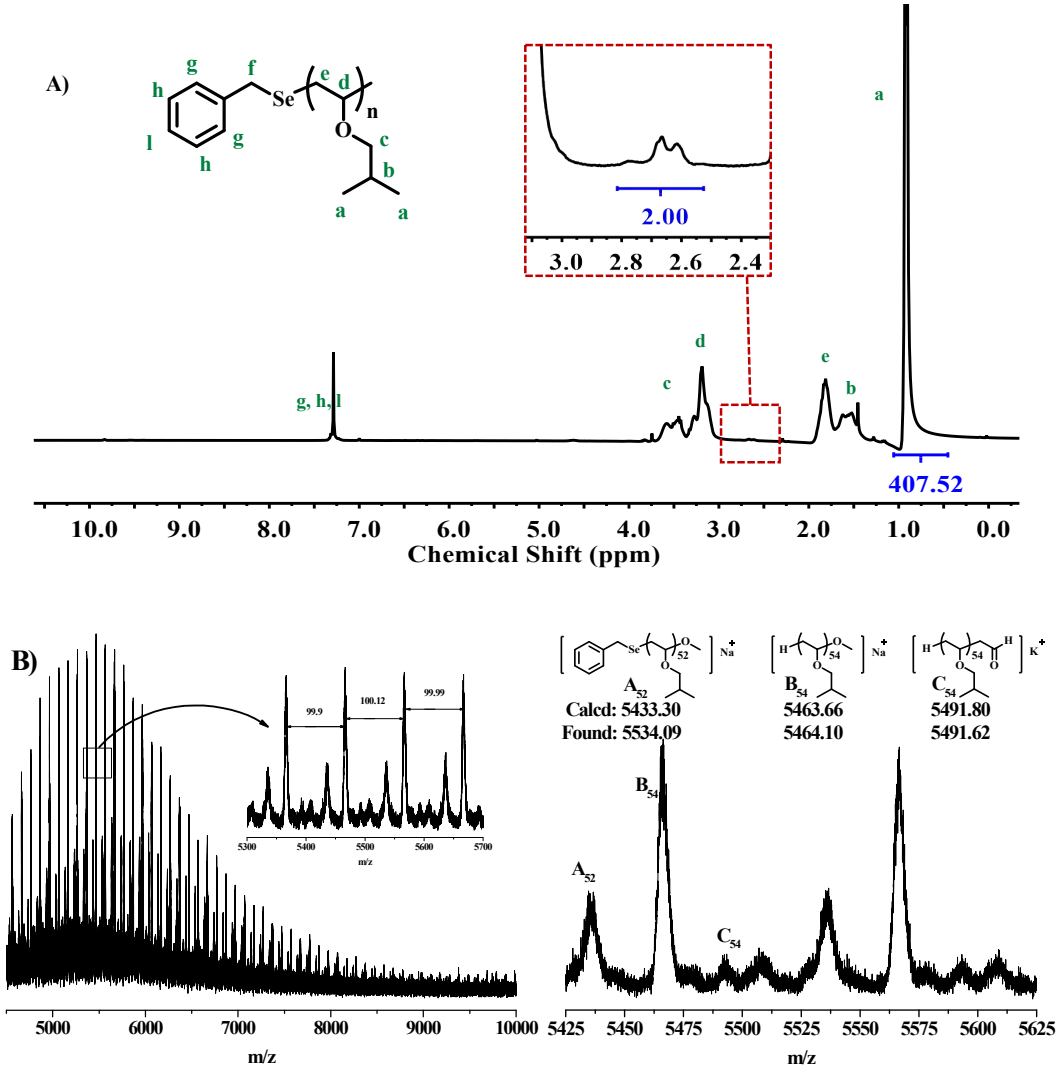


Figure S9. Bulk polymerization results of IBVE with the molar ratio $[IBVE]_0$: $[BnSeBr]_0$: $[Mn(CO)_5Br]_0$ = 50 : 1 : 0.1 at 25 °C, A) ^1H NMR spectra analysis($M_{n,NMR}$ = 7100 g mol^{-1}). B) MALDI-TOF MS of PIBVE ($M_{n,SEC}$ = 7800 g mol^{-1}, $Đ$ = 1.18).

Table S5. Bulk polymerization of IBVE with EBSeBr as initiator at 25 °C.

Entry	$[IBVE]_0 : [EBSeBr]_0 : [Mn(CO)_5Br]_0$	Time	Conv.%	[a] $M_{n,th}$ (g mol^{-1})	[b] $M_{n,SEC}$ (g mol^{-1})	$Đ$
1	50 : 1 : 0.05	62 h	85.9	4500	4700	1.19
2	100 : 1 : 0.1	47 h	74.4	7600	8400	1.25
3	200 : 1 : 0.2	40 h	75.6	15300	21100	1.16
4	100 : 1 : 0	24 h	-	-	-	-

[a] Calculated based on conversion ($M_{n,th}$ = $[M]_0/[BnSeBr]_0$ × conversion × M + M_{EBSeBr}).
[b] Determined by SEC using polystyrene (PS) as standard in tetrahydrofuran (THF).

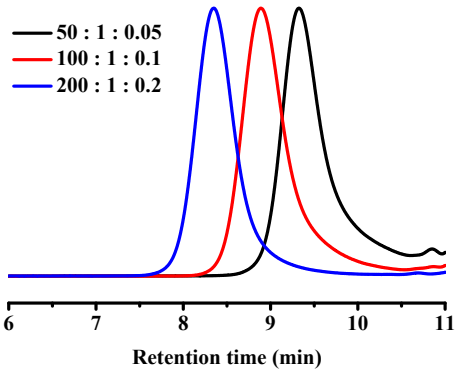


Figure S10. SEC traces of PIBVE with EBSeBr as initiator under various rates.

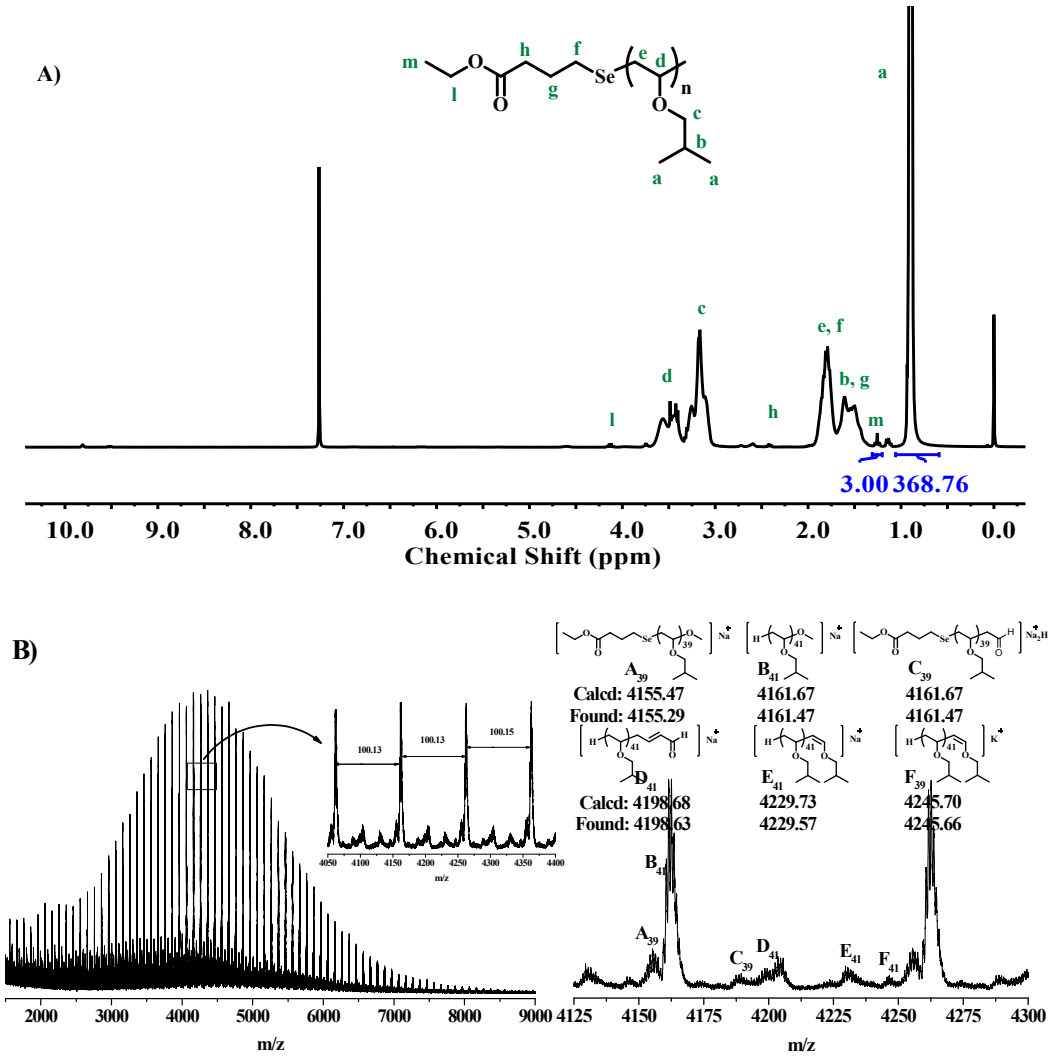
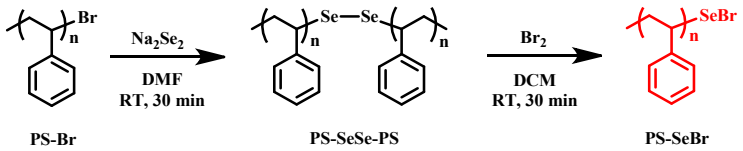


Figure S11. Bulk polymerization results of IBVE with the molar ratio $[IBVE]_0 : [EBSeBr]_0 : [Mn(CO)_5Br]_0 = 50 : 1 : 0.05$ at 25 °C, A) ^1H NMR spectra analysis($M_{n,NMR}$ = 6400 g mol^{-1}). B) MALDI-TOF MS of PIBVE ($M_{n,SEC}$ = 6600 g mol^{-1}, $Đ$ = 1.09).



Scheme S1. Synthetic routes of macroinitiator (PS-SeBr).

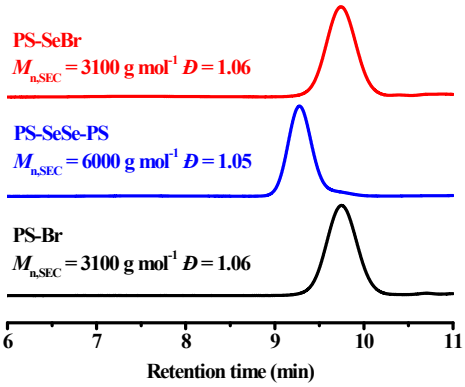


Figure S12. SEC traces of the synthesis of macroinitiator (PS-SeBr).

Table S6 Polymerization of IBVE with PS-SeBr as initiator at 25 °C, V_{IBVE} = $V_{toluene}$ = 0.25 mL.

Entry	$[IBVE]_0$: $[PS\text{-}SeBr]_0$: $[Mn(CO)_5Br]_0$	Time	Conv.%	[a] $M_{n,th}$ (g mol^{-1})	[b] $M_{n,SEC}$ (g mol^{-1})	Đ
1	200 : 1 : 0.2	11 h	85.4	20100	22100	1.16
4	200 : 1 : 0	24 h	-	-	-	-

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

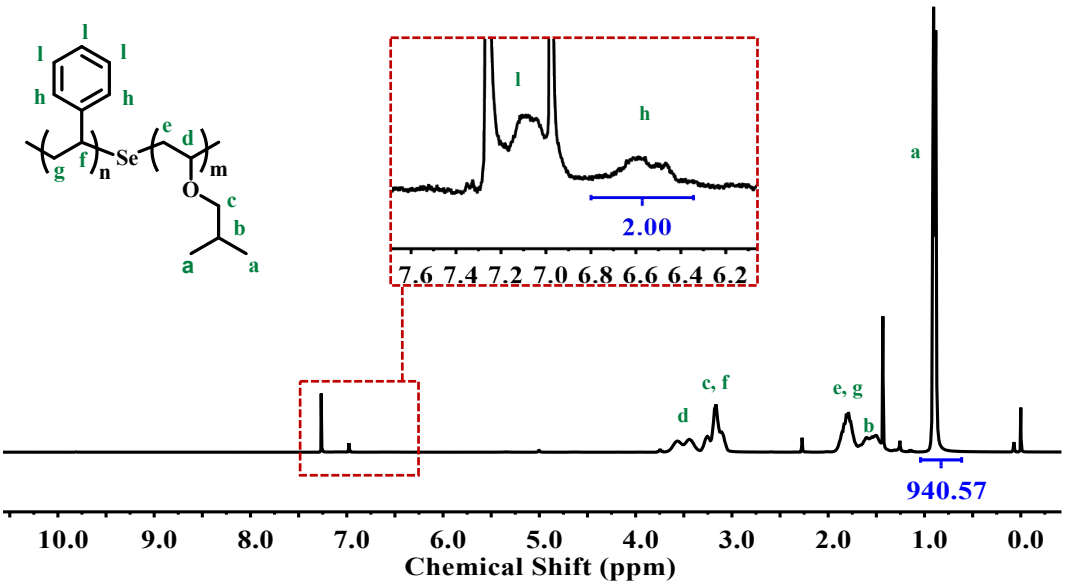


Figure S13. ^{1}H NMR spectra analysis of PS-*b*-PIBVE ($M_{n,NMR}$ = 18800 g mol^{-1}).

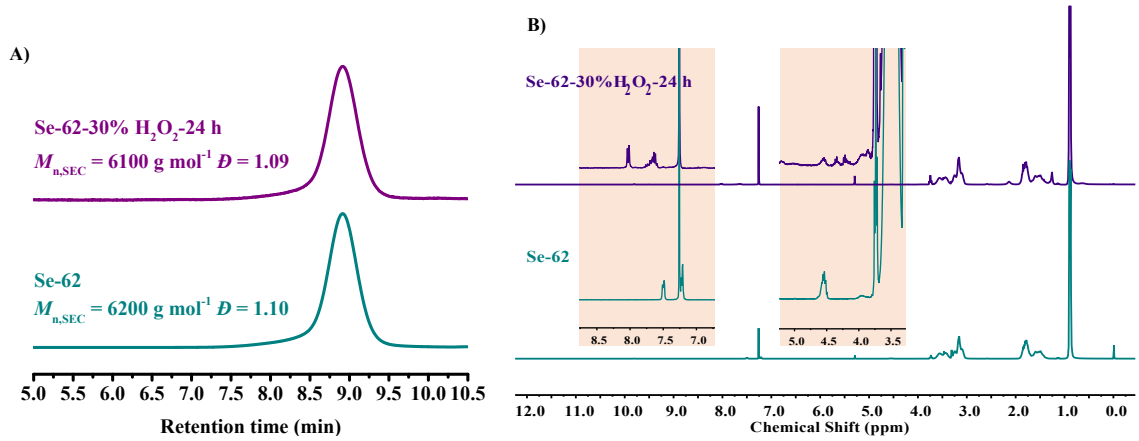


Figure S14. A) SEC traces; B) ^{1}H NMR spectra analysis of PIBVE before and after oxidation.