Electronic Supplementary Material (ESI) for Polymer Chemistry.

Synthesis of Selenide-containing Polymers by Multicomponent Polymerization Based on γ -Butyroselenolactone

Methods

NMR

^{1}H and ^{13}C-NMR spectra were recorded in $CDCl_3$ or DMSO-*d*^{6} on a Bruker Avance 300 at 300/75 MHz or on a Bruker Avance 400 at 400/100 MHz. Chemical shifts are presented in parts per million (δ) relative to $CDCl_3$ (7.26 ppm in ^{1}H- and 77.00 ppm in ^{13}C-NMR respectively) as internal standard or relative to diphenyl selenide (416.00 ppm) in ^{77}Se NMR. Coupling constants (J) in ^{1}H-NMR are given in Hz. The resonance multiplicities are described as *s* (single), *d* (doublet), *t* (triplet), q (quartets) or *m* (multiplet).

GPC

Both the number-average molecular weight ($M_{n,GPC}$) and molecular weight distribution (*Đ*) of all the polymers were determined by TOSOH HLC-8320 gel permeation chromatograph (GPC) equipped with a refractive-index detector (THF), using TSK gel Multi pore HZ-N (3) 4.6 × 150 mm column and a RI detector at 40℃. THF was used as the eluent at a flow rate of 0.35 mL min^{-1}. All the GPC samples were injected using a TOSOH plus auto sampler and the molar masses were calibrated with narrow polydispersity using polystyrene or poly (methyl methacrylate) standards followed by a universal calibration.

FTIR

Fourier transform infrared (FT-IR) spectra were measured on a Bruker TENSOR 27 FT-IR spectrometer (KBr disk).

UV-Irradiation

UV−vis spectra were recorded on a Shimadzu UV-3150 spectrophotometer (Shimadzu China, Shanghai, China).

MALDI-TOF-MS

MALDI-TOF mass spectroscopy (MS) were acquired on an UltrafleXtreme MALDI TOF mass spectrometer (Bruker Daltonics, Germany) equipped with an Nd:YAG smart beam-II laser with 355-nm wavelength and 200 Hz firing rate. For high resolution mass analysis the instrument was operated in the reflector mode. MS data were further processed using FlexAnalysis 1.3 software package.

TGA

Thermogravimetric analysis (TGA) was carried out on a TG/DTA 6300 Instruments with a heating rate of 10 ℃/min from the room temperature to 800 ℃ under nitrogen atmosphere.

DSC

Differential scanning calorimeter (DSC) was carried out on a DSC2010 Instruments with a heating rate of 10 ℃/min from -70 ℃ to 40 ℃

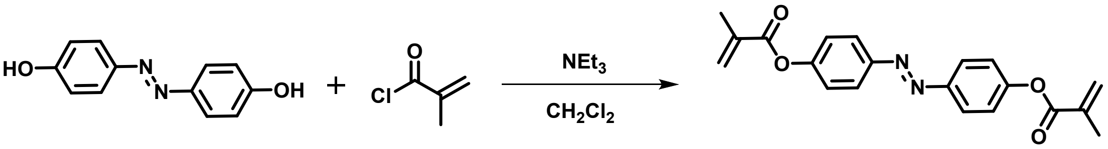
ICP

Inductively Coupled Plasma (ICP) was carried out on Agilent Technologies 5110 ICP-OES.

Materials

4,7,10-trioxa-1,13-tridecanediamine, Aldrich, 97% , Shanghai China ; tributylphosphine, Aladdin, 95%, Shanghai China; ethylene glycol dimethacrylate, Alfa aesar, 98%, Shanghai China; pyrenemethylamine hydrochloride, Aldrich, 95%, Shanghai China; 1,3-bis(aminopropy) tetramethyldisiloxane, Energy chemical, 97%, Shanghai China; polyoxyethylene bis(amine), Aladdin, M.W. 1000, Shanghai China; α,α′ dichloro-p-xylene, Energy chemical, 98%, Shanghai China; α,α'-dibromo-p-xylene, 9 Ding chemical, 98%, Shanghai China; 1,6-diiodohexane, Adamas-beta, 98%,Shanghai China ; triethylamine, Enox ,99%+, Jiangsu China ; 9,9-bis(4-glycidyloxyphenyl)fluorine, Tokyo Chemical Industry (TCI), 98%, Shanghai, China; 4,4'-dihydroxyazobenzene, HWRK Chem Co.Ltd., Beijing, China; methacryloyl chloride, Energy chemical, 97%, Shanghai China; tetrahydrofuran (THF), Oceanpak, 99.9%, Sweden; dimethylformamide (DMF), Oceanpak, 99.9%, Sweden; hexane and chloroform ($CHCl_3$) were purchased from Enox (Jiangsu China).

Synthesis of diazene-1, 2-diylbis (4, 1-phenylene) bis (2-methylacrylate) (P4-MMA)



1.1 g (5.0 mmol) of 4,4'-dihydroxyazobenzene and 2.1 g (21.0 mmol) of triethylamine were dissolved in 30 ml of dehydrated CH_2Cl_2 and 1.1 g (10.5 mmol) of methacryloyl chloride was added to it dropwise using a dropping funnel at 0 °C in an ice bath. The reaction mixture was then stirred at room temperature for 24 h. After the reaction time had lapsed, the reaction mixture was filtered, and the solvent was evaporated, and the crude product was purified by silica gel column chromatography using petroleum ether/ethyl acetate (20:1 v/v) as eluent.

Characterization data for diazene-1, 2-diylbis (4, 1-phenylene) bis (2-methylacrylate) (P4-MMA): A yellow solid was obtained in 48% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.97 (d, J = 8.8 Hz, 4H), 7.29 (d, J = 8.8 Hz, 4H), 6.39 (s, 2H), 5.80 (s, 2H), 2.09 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.52 (s), 153.01 (s), 150.13 (s), 135.70 (s), 127.70 (s), 124.09 (s), 122.30 (s), 18.39 (s).

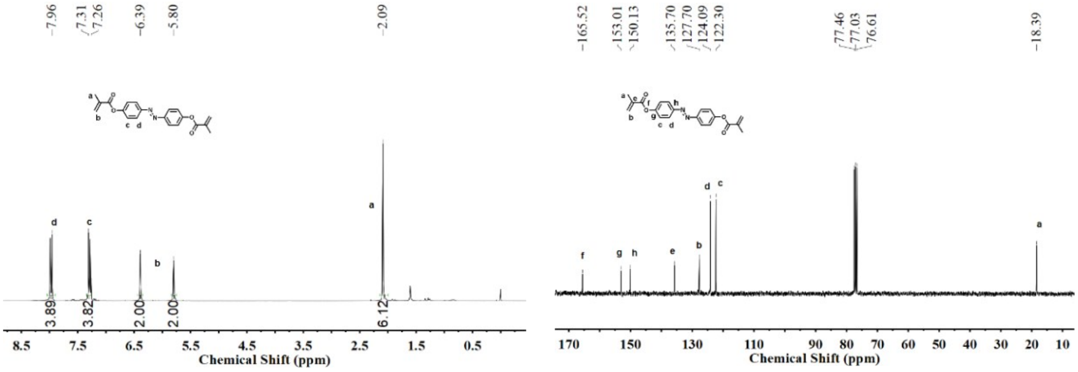
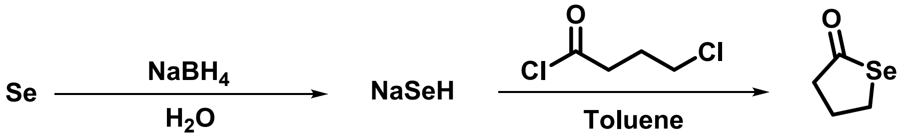


Figure S1. ^{1}H NMR and ^{13}C NMR spectra of P4-MMA in $CDCl_3$.

Synthesis of γ-butyroselenolactone



γ-Butyroselenolactone was synthesized following a literature procedure.[1] The reaction was conducted under Argon atmosphere. 16.0 g (200 mmol) of selenium and 250 ml water was added to 1000 ml three-necked flask. 15.2 g (400mmol) $NaBH_4$ was dissolved in 150 ml water and was added to three-necked flask dropwise using a dropping funnel in an ice bath. The reaction mixture was stirred at room temperature for 1 h. Then 2.56 g Bu_4HSO_4 dissolved in 10 ml water was added to three-necked flask as phase transfer agent. 28.2 g (200 mmol) 4-chlorobutanoyl chloride dissolved in 400 ml toluene and was added to three-necked flask dropwise using a dropping funnel. The reaction mixture was stirred at room temperature for 12 h. Then, 200 ml 5% $NaHCO_3$ solution was added to three-necked flask. The reaction mixture was stirred at room temperature for 4 h. The reaction mixture was filtered. The organic phase was washed with water, the aqueous phase was extracted with ethyl acetate, and the organic phase was merged. Then the solvent was evaporated, and the crude product was purified by vacuum distillation.

Characterization data for γ-butyroselenolactone (BSeL). A colorless liquid was obtained in 70% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.60 – 3.38 (m, 2H), 2.42 (t, J = 6.9 Hz, 2H), 2.30 – 2.11 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 46.84 (s), 29.92 (s), 26.60 (s).

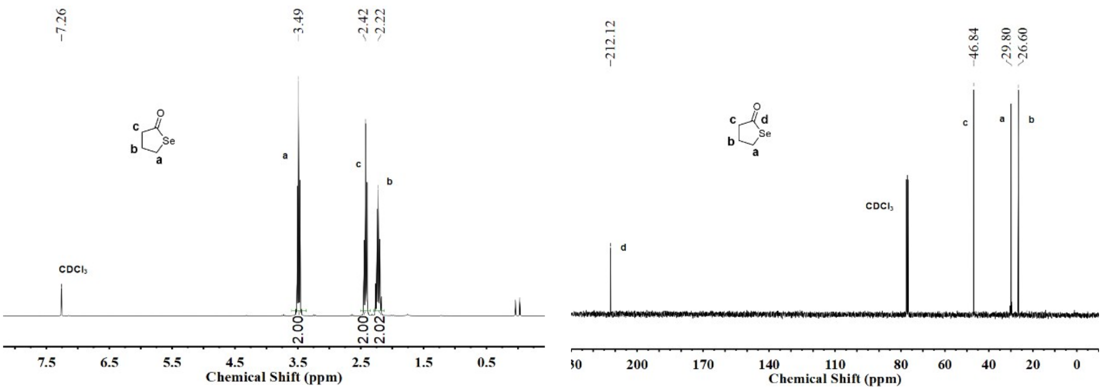
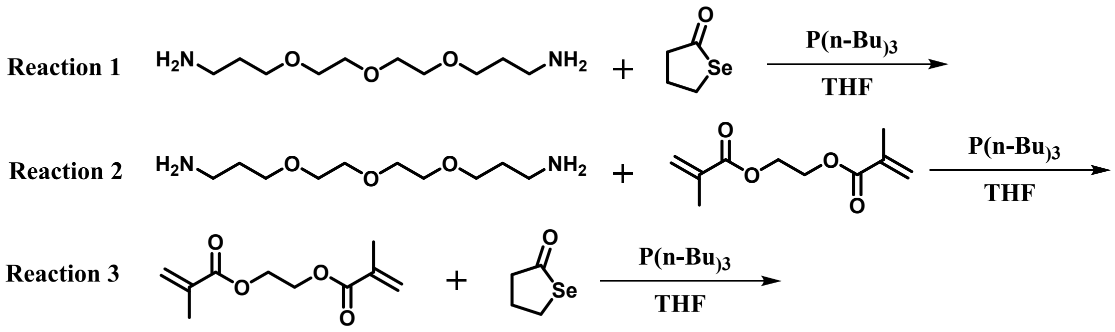


Figure S2. ^{1}H NMR and ^{13}C NMR spectra of BSeL in $CDCl_3$.

Control experiment



All the reactions were conducted under argon atmosphere at room temperature.

Reaction 1:

Into a 25 mL Schlenk tube equipped with a magnetic stir bar was added a THF solution (5 mL) of 4,7,10-trioxa-1,13-tridecanediamine (1102 mg, 5 mmol) and P(n-Bu)$_3$ (202 mg, 1 mmol). After oxide-eliminating, γ-butyroselenolactone (1500 mg, 10 mmol) was added slowly. The solution was stirred for 24 h at room temperature.

Reaction 2:

Into a 25 mL Schlenk tube equipped with a magnetic stir bar was added a THF solution (5 mL) of 4,7,10-trioxa-1,13-tridecanediamine (1102 mg, 5 mmol), ethylene glycol dimethacrylate (992 mg, 5 mmol) and P(n-Bu)$_3$ (202 mg, 1 mmol). After oxide-eliminating, the solution was stirred for 24 h at room temperature.

Reaction 3

Into a 25 mL Schlenk tube equipped with a magnetic stir bar was added a THF solution (5 mL) of γ-butyroselenolactone (1500 mg, 10 mmol), ethylene glycol dimethacrylate (992 mg, 5 mmol) and P(n-Bu)$_3$ (202 mg, 1 mmol). After oxide-eliminating, the solution was stirred for 24 h at room temperature.

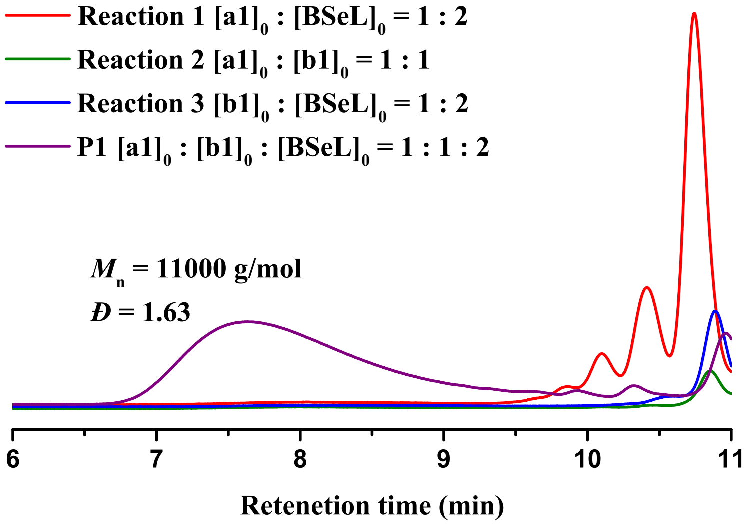


Figure S3. GPC curves of Reaction 1, Reaction 2 and Reaction 3

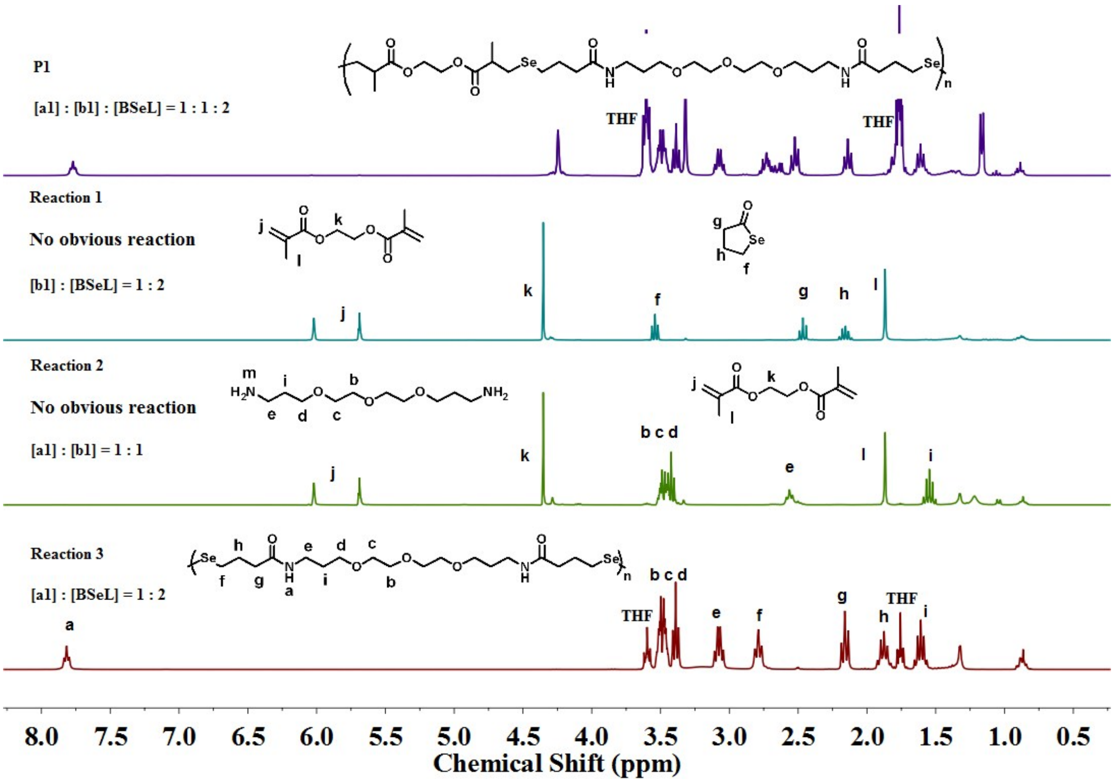
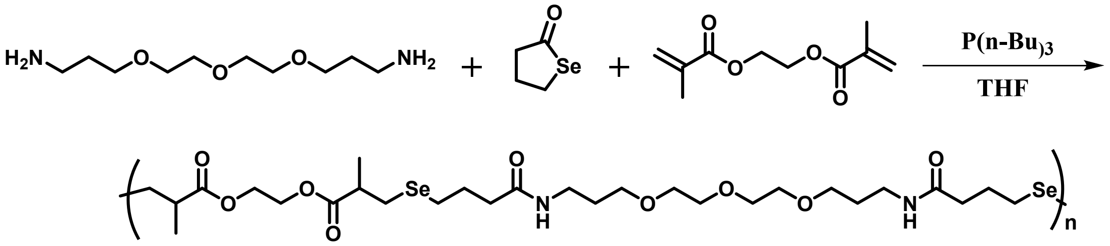


Figure S4. ^{1}H NMR of Reaction 1, Reaction 2 and Reaction 3 in DMSO-d_6

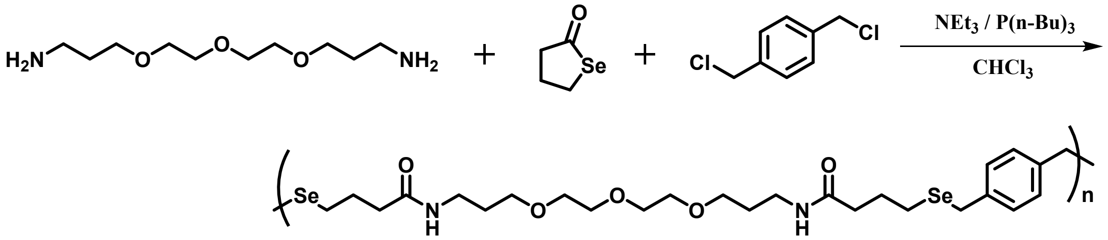
General procedure for polymers

One-pot stepwise polymerization of the γ-Butyroselenolactone, diamine and dimethacrylate



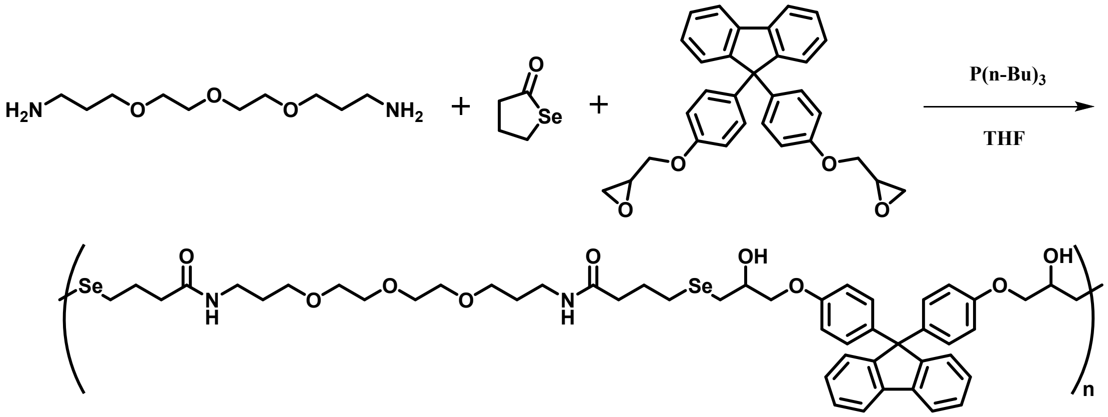
Without additional notes, a typical procedure of the polymerization of polymer-1 (P1) is given below as an example. All the polymerization were conducted under Argon atmosphere at room temperature. Into a 25 mL Schlenk tube equipped with a magnetic stir bar was added a THF solution (3 mL) of 4,7,10-trioxa-1,13-tridecanediamine (1102 mg, 5 mmol) and P(n-Bu)$_3$ (202 mg, 1 mmol). After oxide-eliminating, γ-Butyroselenolactone (1500 mg, 10 mmol) was added slowly. Then a THF solution (2 mL) of ethylene glycol dimethacrylate (992 mg, 5 mmol) was added into the tube. The solution was stirred for 24 h at room temperature, and the solution was precipitated in cold diethyl ether. Finally, the polymer was dried overnight in a vacuum oven at 40 ^{o}C.

One-pot stepwise polymerization of the γ-Butyroselenolactone, diamine and dihalogenated hydrocarbon



γ-Butyroselenolactone was synthesized following a literature procedure.[1] Without additional notes, a typical procedure of the polymerization of polymer-6 (P6) is given below as an example. All the polymerization were conducted under Argon atmosphere at room temperature. Into a 25 mL Schlenk tube equipped with a magnetic stir bar was added a CHCl$_3$ solution (3 mL) of 4,7,10-trioxa-1,13-tridecanediamine (220 mg, 1 mmol) NEt$_3$ (233 mg, 2.3 mmol)and P(n-Bu)$_3$ (40 mg, 0.2 mmol). After oxide-eliminating, γ-Butyroselenolactone (300 mg, 2 mmol) was added slowly. Then a CHCl$_3$ solution (2 mL) of 1,4-Bis(chloromethyl)benzene (175 mg, 1 mmol) was added into the tube. The solution was stirred for 24 h at room temperature, and the solution was precipitated in cold diethyl ether, pured by Water and acetone and obtained via filtration. Finally, the polymer was dried overnight in a vacuum oven at 40 °C.

One-pot stepwise polymerization of the selenolactone, diamine and 9, 9-Bis(4-glycidyloxyphenyl)fluorine



Without additional notes, a typical procedure of the polymerization of polymer-9 (P9) is given below as an example. All the polymerization were conducted under Argon atmosphere at room temperature. Into a 25 mL Schlenk tube equipped with a magnetic stir bar was added a THF solution (3 mL) of 4,7,10-trioxa-1,13-tridecanediamine (220 mg, 1 mmol) and P(n-Bu)$_3$ (40 mg, 0.2 mmol). After oxide-eliminating, γ-Butyroselenolactone (300 mg, 2 mmol) was added slowly, and the solution was stirred for 1h at room temperature. Then a THF solution (2 mL) of 9,9-Bis(4-glycidyloxyphenyl)fluorine (463 mg, 1 mmol) was added into the tube. The solution was stirred for 24 h at room temperature, and the solution was precipitated in cold diethyl ether. Finally, the polymer was dried overnight in a vacuum oven at 40 °C.

Determine Terminal Group (Primary amino group) of P1-A

P1-A dissolved in 10 ml of dehydrated CHCl$_3$ and excess 1, 6-diiodohexane was added to it. The reaction mixture was then stirred at 60 °C for 24 h. Then the solution was precipitated in cold diethyl ether. Finally, the polymer was dried overnight in a vacuum oven at 40 °C.

Determine Terminal Group (Selenol group) of P1-B

P1-B dissolved in 10 ml of dehydrated THF (2 mg/mL), excess butanethiol was added to it. The solution was stirred for 1 h at room temperature.

Determine Terminal Group (Double bond group) of P1-C

γ-Butyroselenolactone was synthesized following a literature procedure.[1] The reaction was conducted under Argon atmosphere at room temperature. Into a 25 mL Schlenk tube equipped with a magnetic stir bar was added a THF/H_2O (1:1 v/v) solution (3 ml) of pyrenemethylamine hydrochloride (94 mg, 0.35 mmol), NaOH(12 mg, 0.31 mmol) and $P(n\text{-}Bu)_3$ (71 mg, 0.35 mmol). After oxide-eliminating, γ-Butyroselenolactone (58 mg, 0.39 mmol) was added slowly. Then a THF solution (2 mL) of P1-C (M_n = 5000 g/mol , 697 mg, 0.14 mol) was added into the tube. The solution was stirred for 24 h at room temperature, and the solution was precipitated in cold diethyl ether. Finally, the polymer was dried overnight in a vacuum oven at 40 ^oC.

Oxidation of P1

P1 dissolved in 10 ml of dehydrated THF (2 mg/mL), excess 3% H_2O_2 was added to it. The solution was stirred for 1 h at room temperature, then was dried with anhydrous Sodium sulphate.

Adsorption of gold ions and palladium ions in solution by P7

Palladium chloride ($PdCl_2$) solutions with palladium ion concentration of 500, 354, 200, 100 and 50 mg/L were obtained by dissolving palladium chloride in hydrochloric acid solution with PH of 1.75. 10 mg P7 was dispersed in 5mL palladium ion solution. Stir at room temperature for 24 hours. Gold chloride ($AuCl_3$) solutions with gold ion concentration of 4000, 3500, 3000, 2500 and 2000 mg/L were obtained by dissolving gold chloride in hydrochloric acid solution with PH of 1.75. 10 mg P7 was dispersed in 5mL gold ion solution. Stir at room temperature for 24 hours.

Characterization

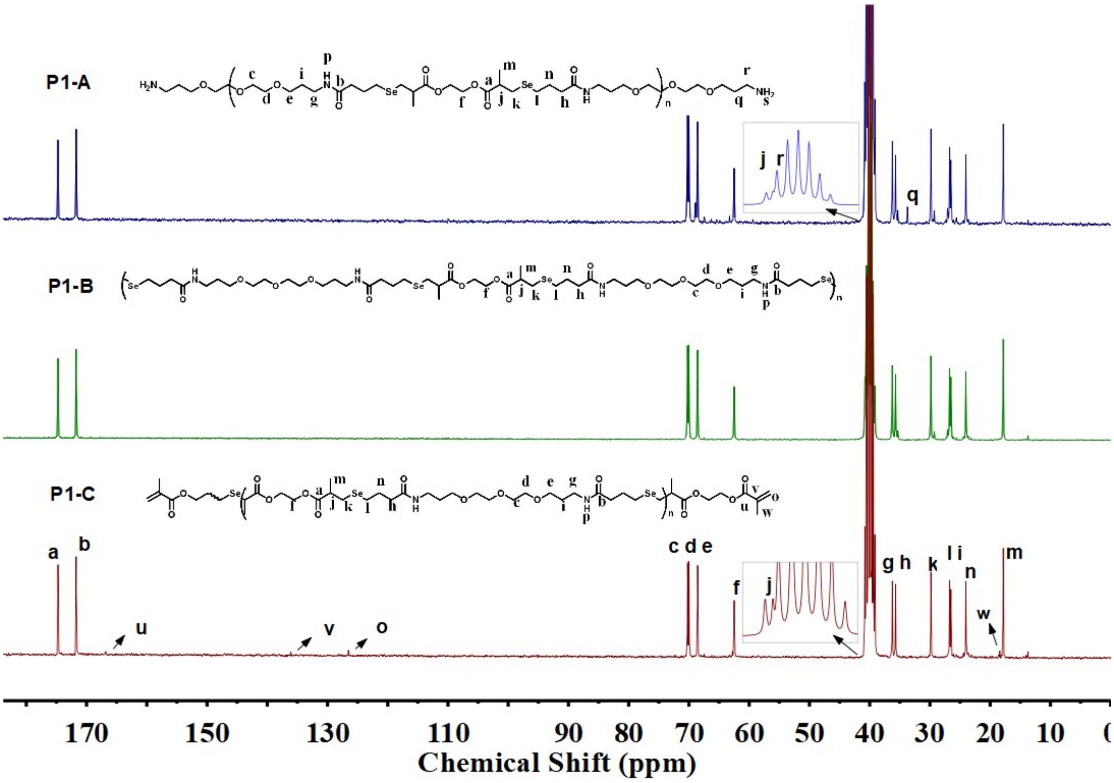


Figure S5. ^{13}C NMR spectra of P1-A, P1-B and P1-C in DMSO-*d*^{6}.

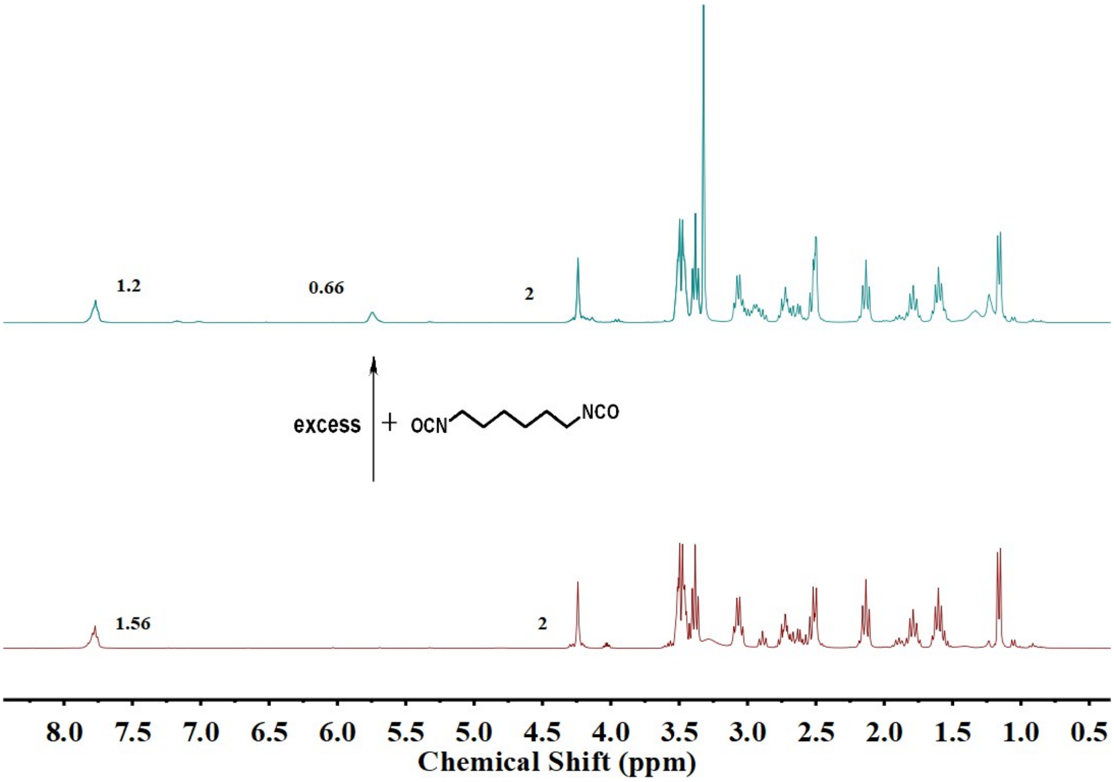


Figure S6. ^{1}H NMR of P1-A and 1, 6-hexamethylene diisocyanate at 60℃ for 48h in DMSO-*d*^{6}.

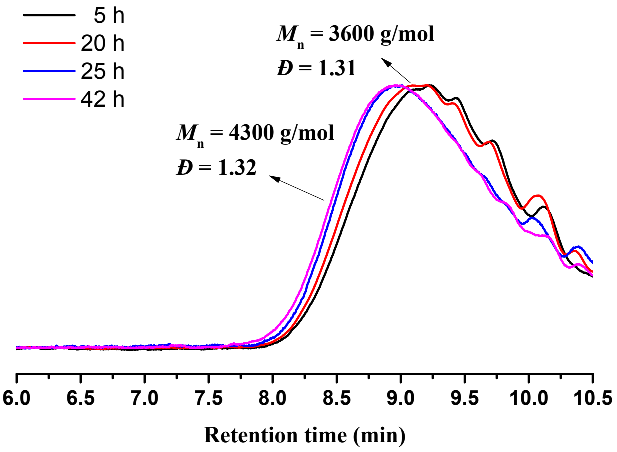


Figure S7. GPC traces of P1-A in THF before and after adding 1, 6-hexamethylene diisocyanate.

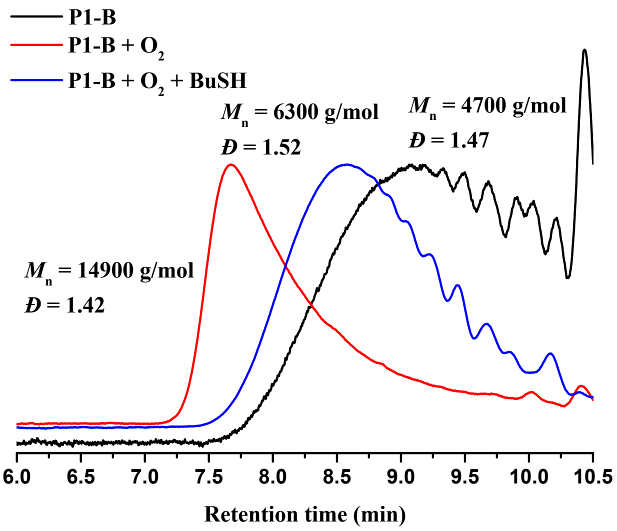
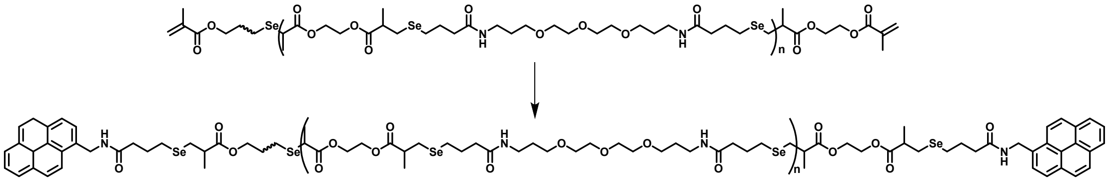


Figure S8. GPC traces of P1-B in THF before and after precipitation(O_2), then add BuSH.



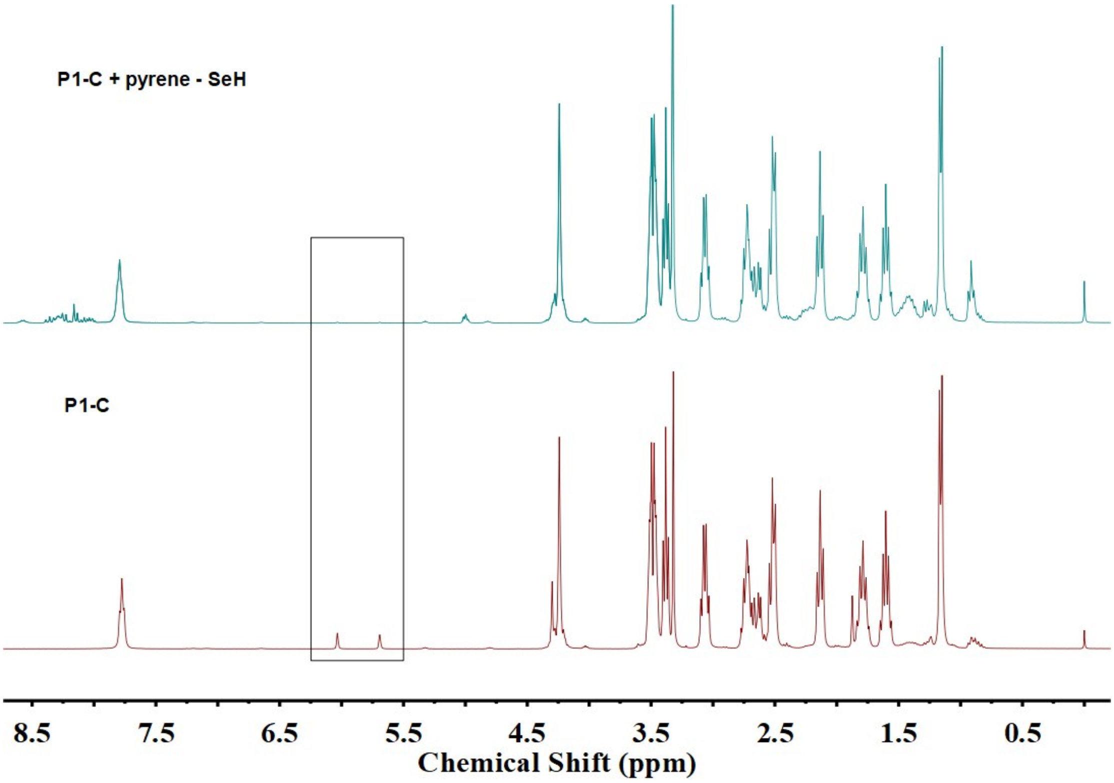
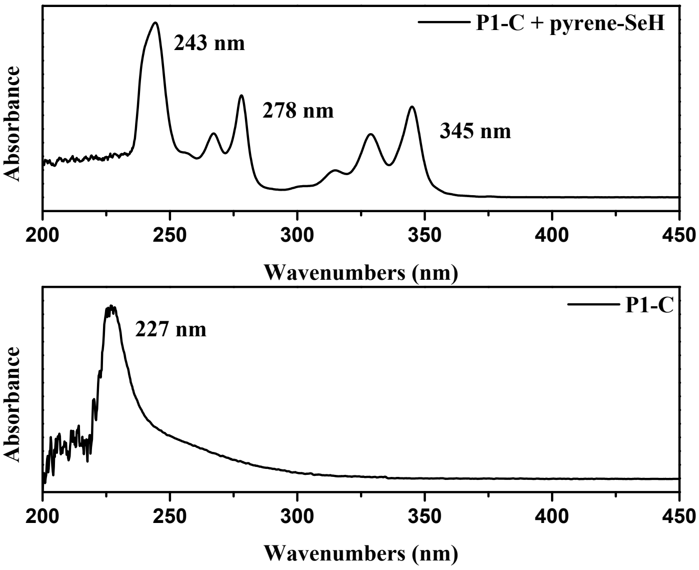
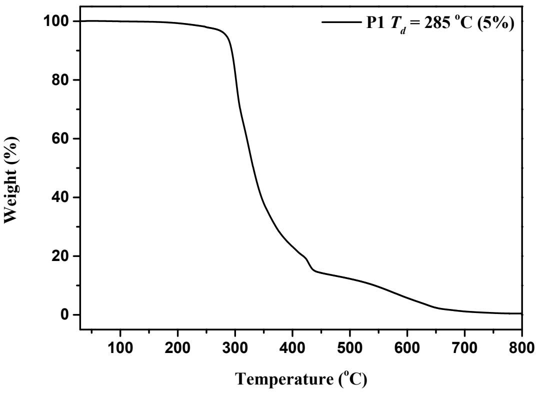


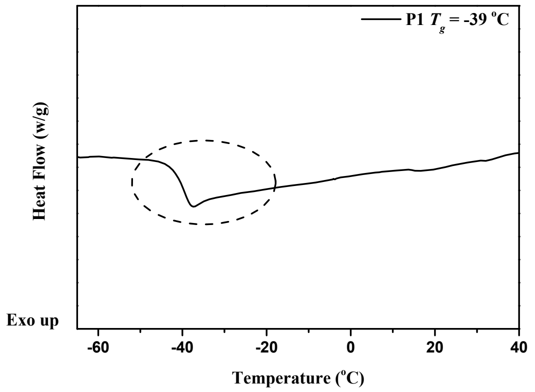
Figure S9. ^{1}H NMR of P1-C and P1-C+pyrene-SeH in DMSO-d^6.



Figue S10. UV of P1-C and P1-C+pyrene-SeH.



Figue S11. Thermogravimetic analysis of P1.



Figue S12. Differential scanning calorimeter of P1.

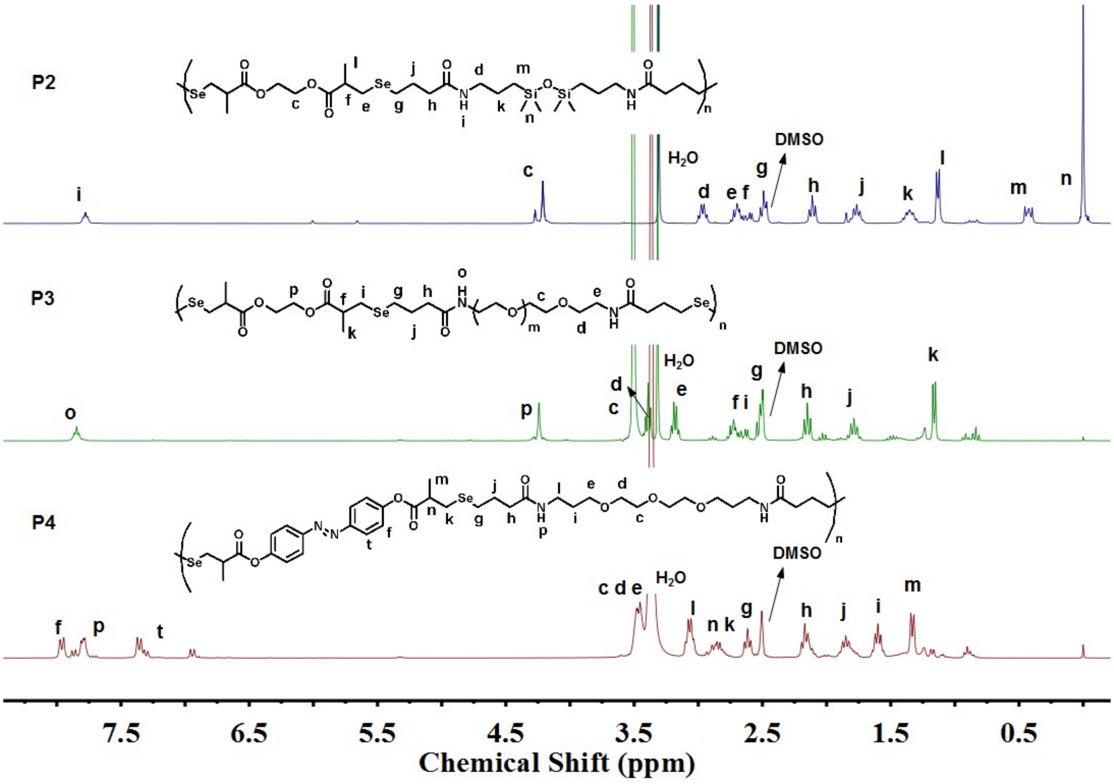


Figure S13. ^{1}H NMR spectra of P2, P3 and P4 in DMSO-*d*^{6}.

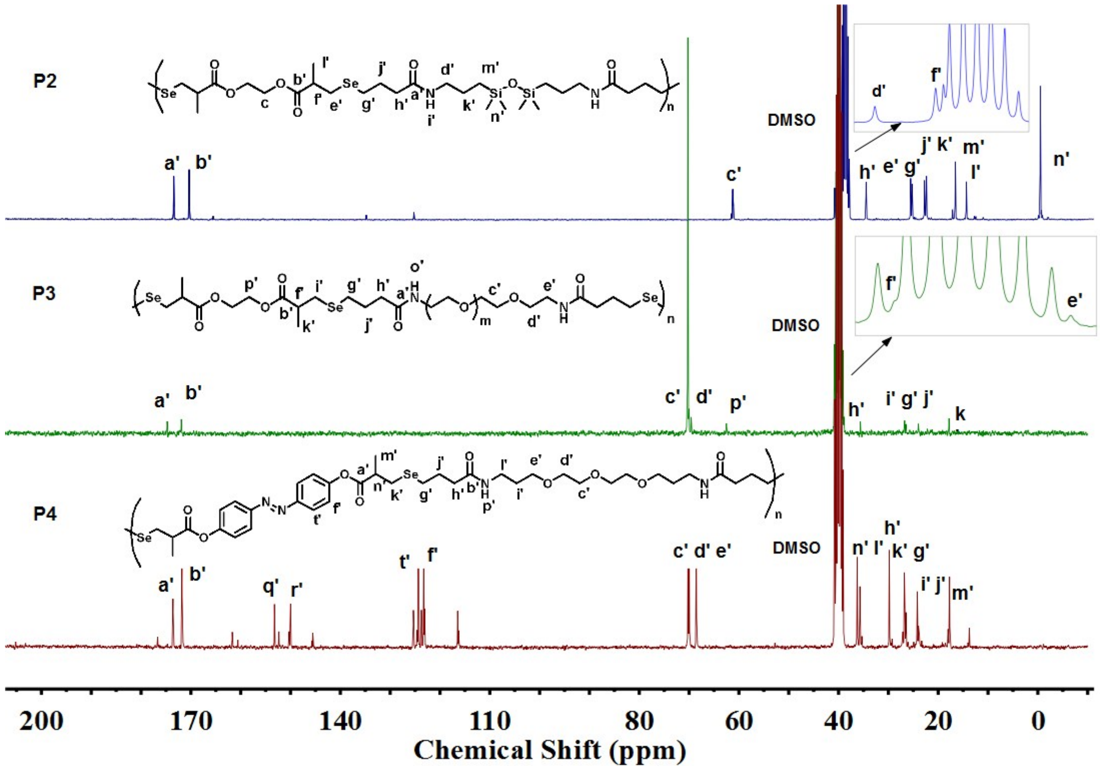


Figure S14. ^{13}C NMR spectra of P2, P3, and P4 in DMSO-*d*^{6}.

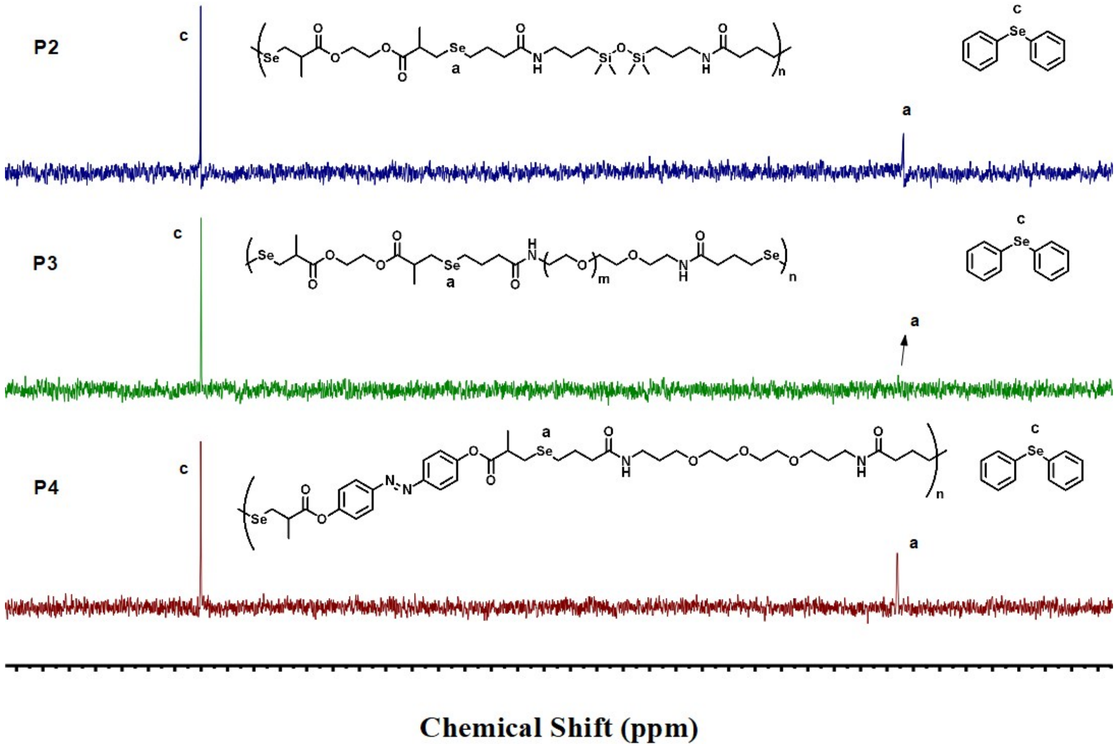


Figure S15. ^{77}Se NMR spectra of P2, P3 and P4 in DMSO-*d*^{6}.

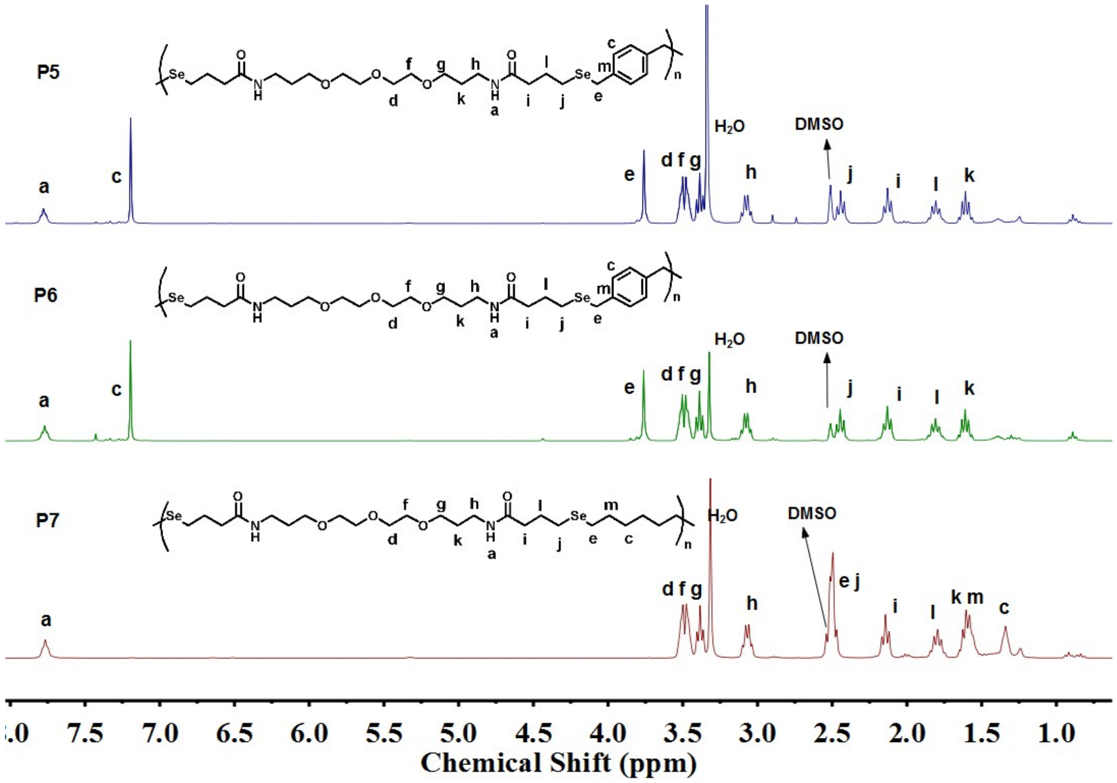


Figure S16. ^{1}H NMR spectra of P5, P6 and P7 in DMSO-d^{6}.

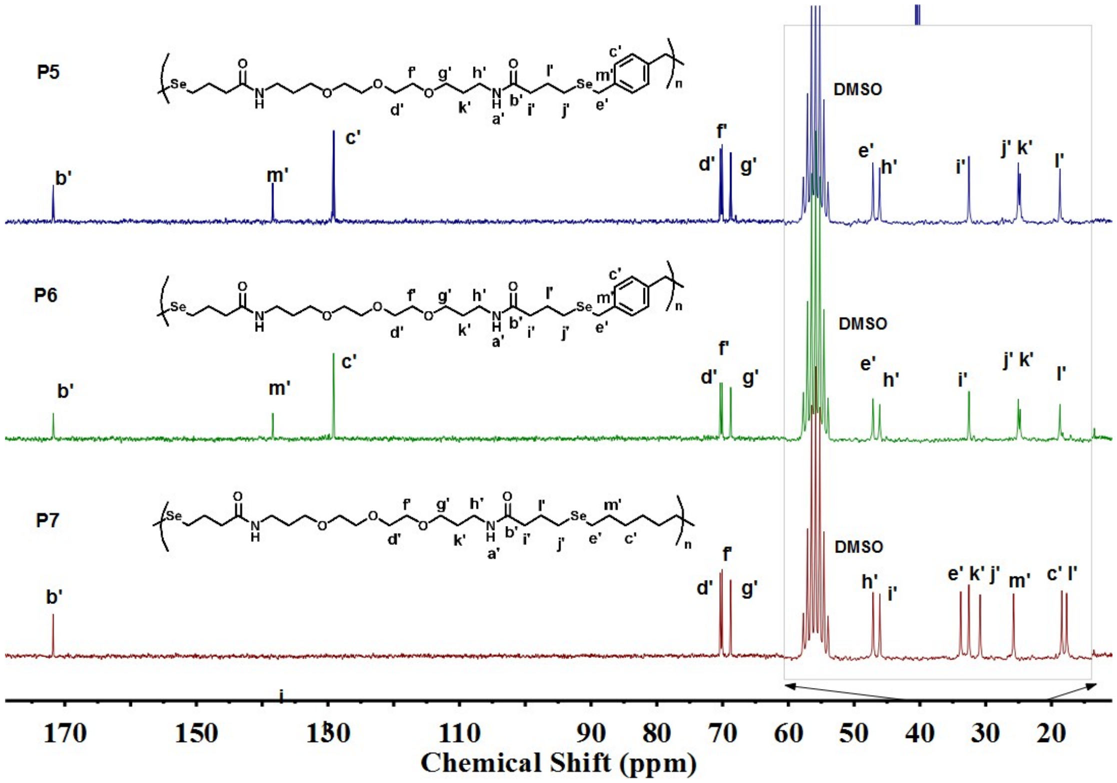


Figure S17. ^{13}C NMR spectra of P5, P6 and P7 in DMSO-d^{6}.

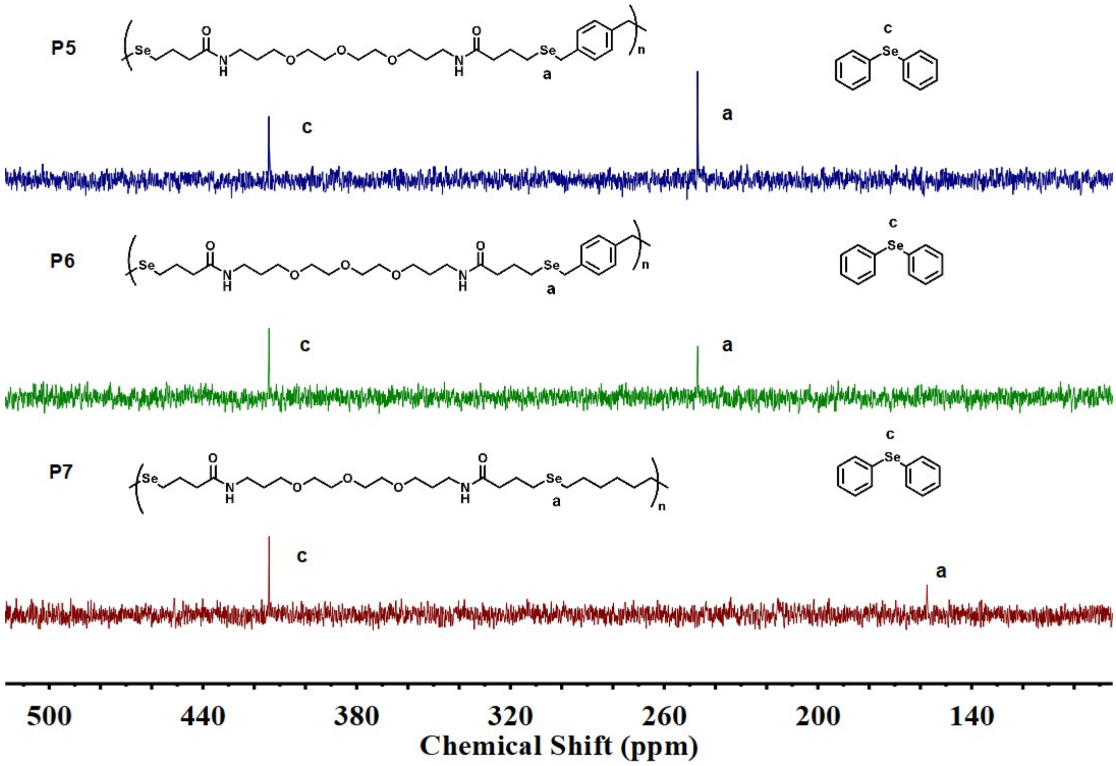


Figure S18. ^{77}Se NMR spectra of P5, P6, and P7 in DMSO-*d*^{6}.

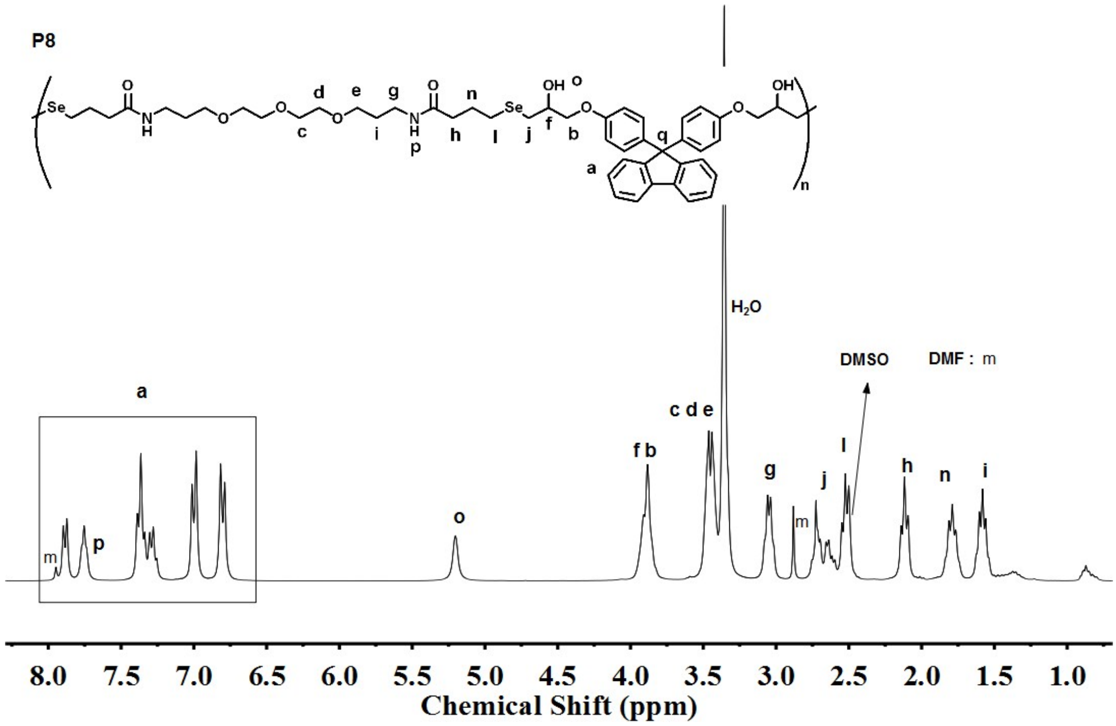


Figure S19. ^{1}H NMR spectra of P8 in DMSO-*d*^{6}.

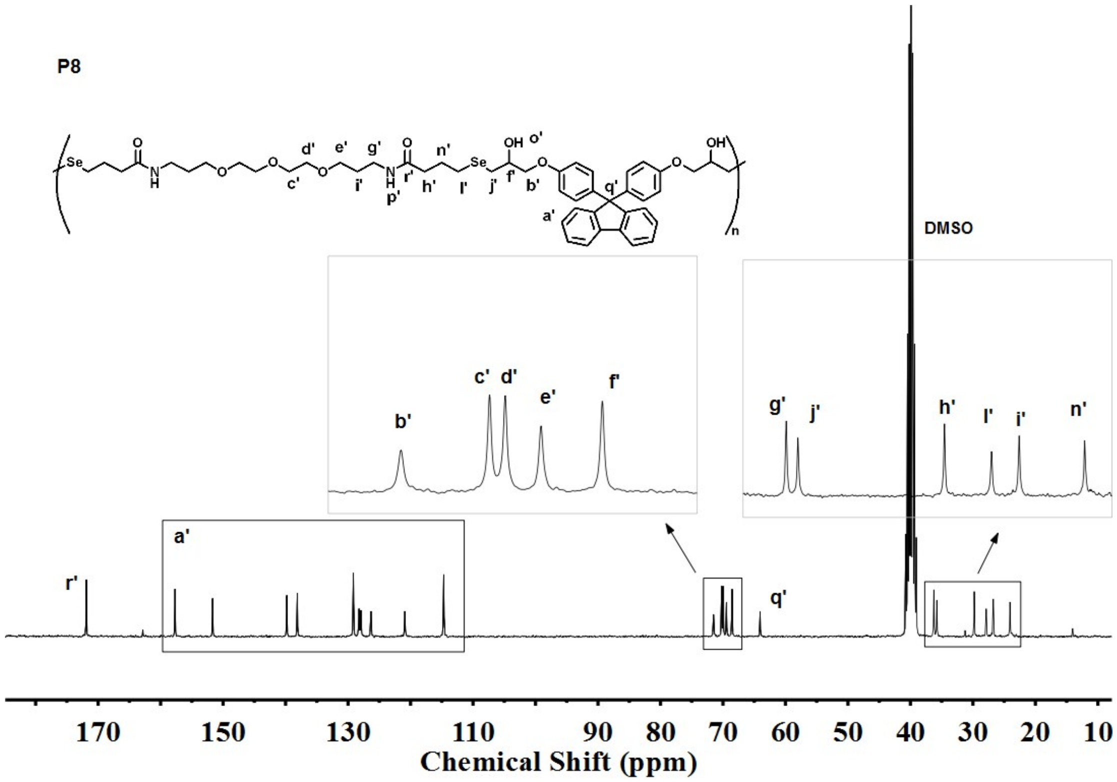


Figure S20. ^{13}C NMR spectra of P8 in DMSO-*d*^{6}.

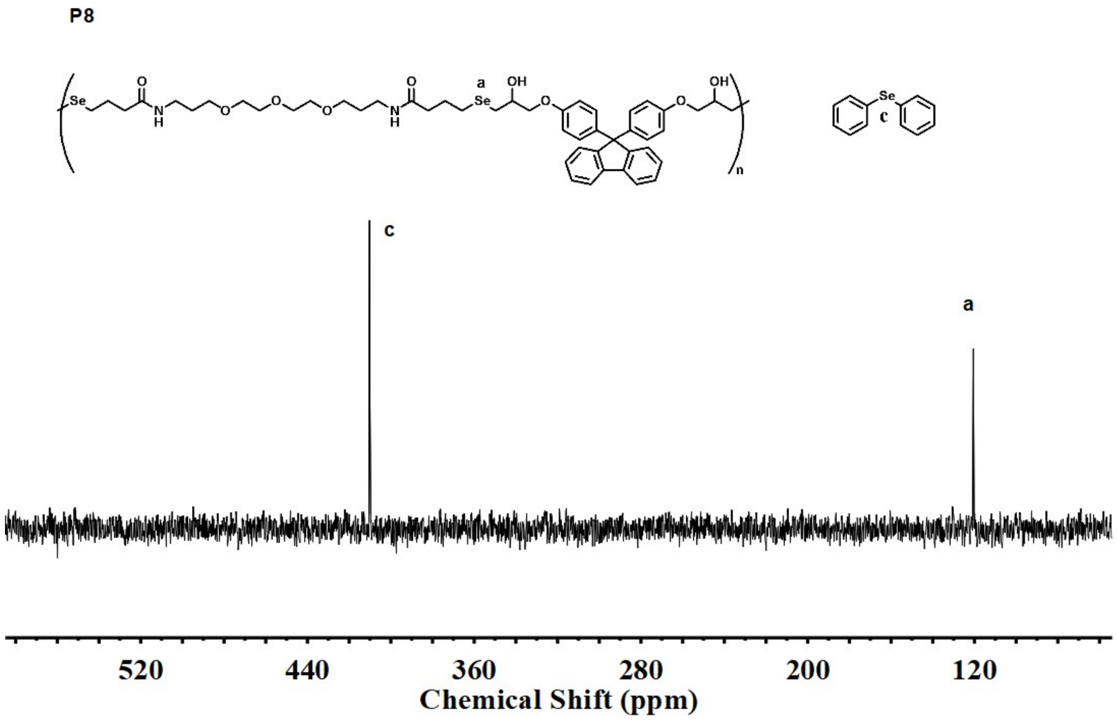


Figure S21. ^{77}Se NMR spectra of P8 in DMSO-*d*^{6}.

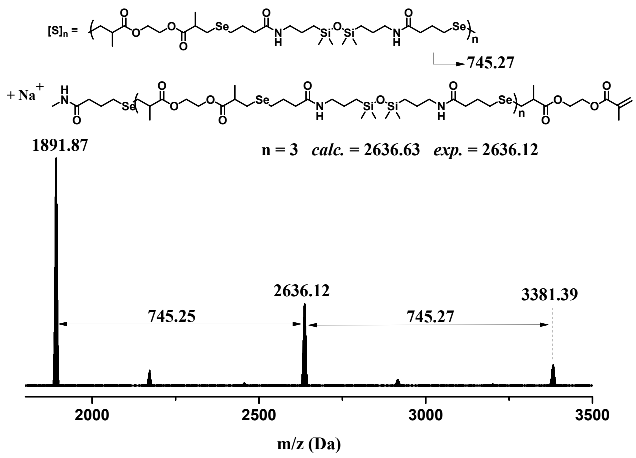


Figure S22. MALDI-TOF-MS spectra of P2 (M_n = 6400 Da, $Đ$ = 1.54).

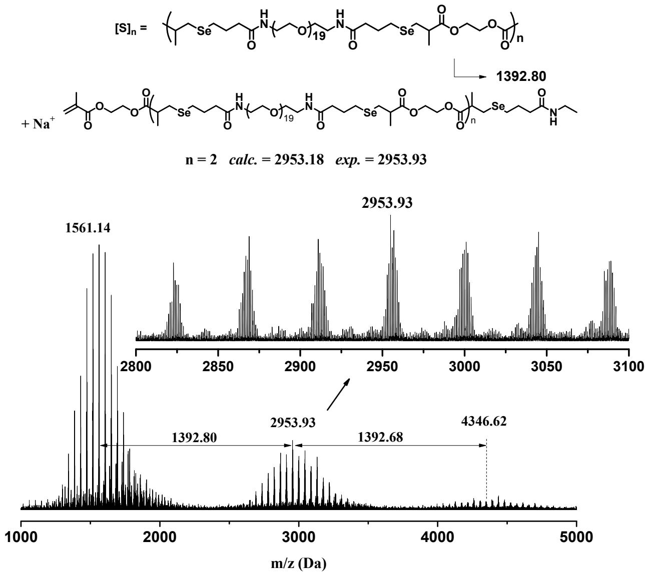


Figure S23. MALDI-TOF-MS spectra of P3 (M_n = 5600 Da, $Đ$ = 1.34).

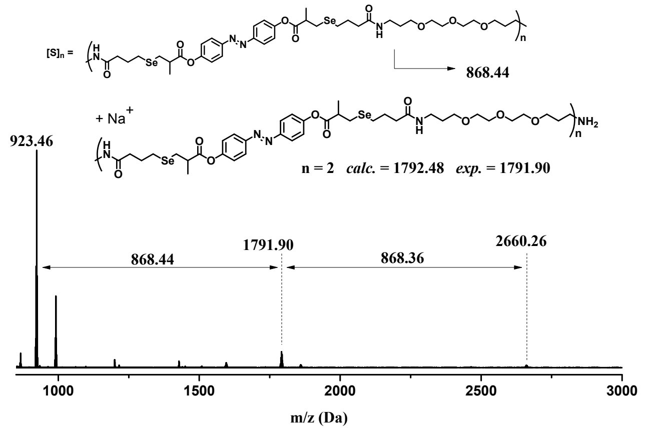


Figure S24. MALDI-TOF-MS spectra of P4 (M_n = 4800 Da, $Đ$ = 1.51).

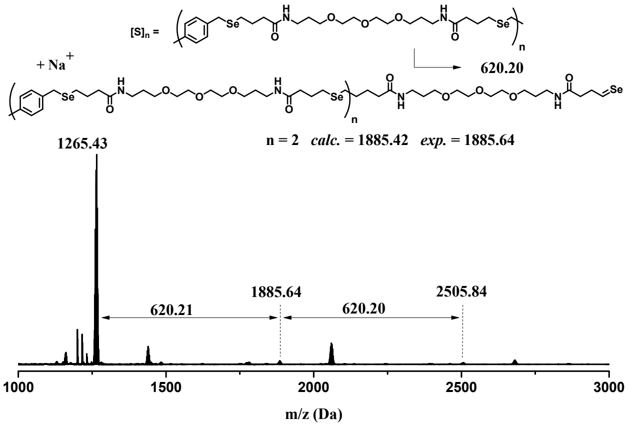


Figure S25. MALDI-TOF-MS spectra of P5 (M_n = 5900 Da, $Đ$ = 1.77).

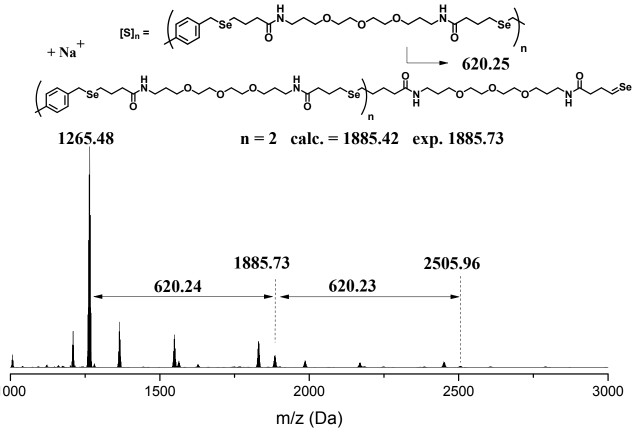


Figure S26. MALDI-TOF-MS spectra of P6 (M_n = 5900 Da, $Đ$ = 1.83).

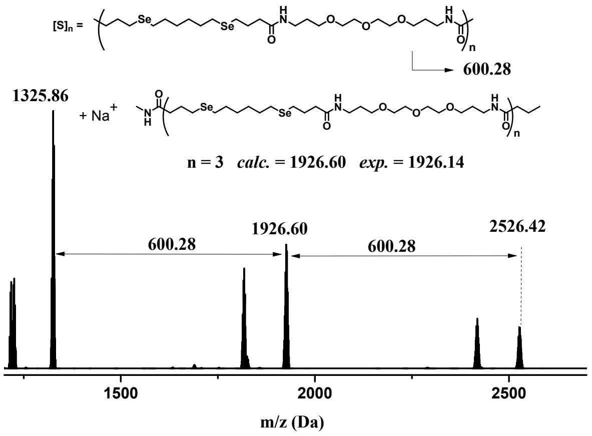


Figure S27. MALDI-TOF-MS spectra of P7 (M_n = 5400 Da, $Đ$ = 1.64).

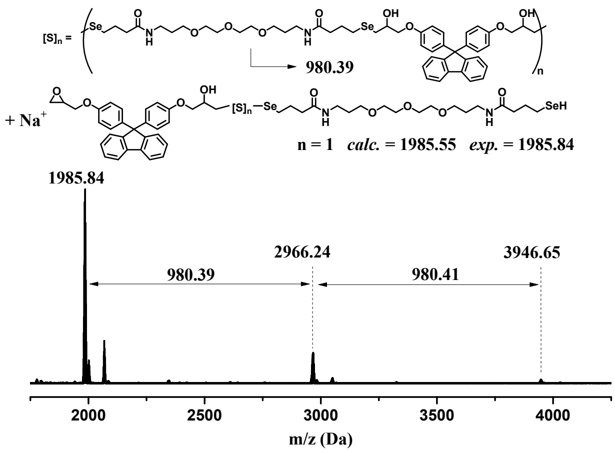


Figure S28. MALDI-TOF-MS spectra of P8 (M_n = 26300 Da, $Đ$ = 2.86).

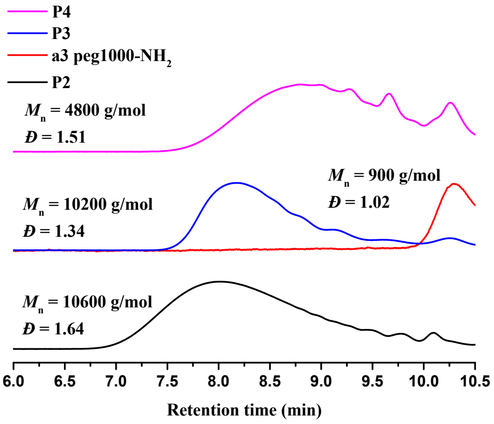


Figure S29. GPC traces of P2, P3, a3 (monomer) and P4 in THF.

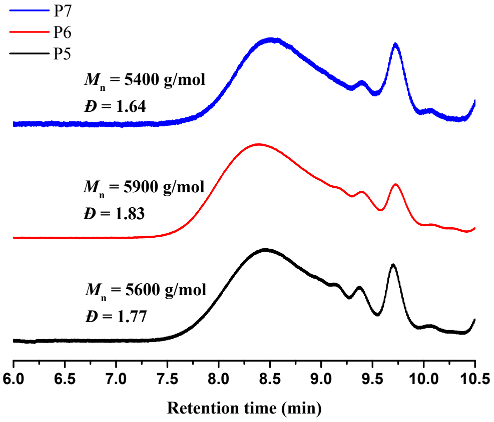


Figure S30. GPC traces of P5, P6 and P7 in DMF.

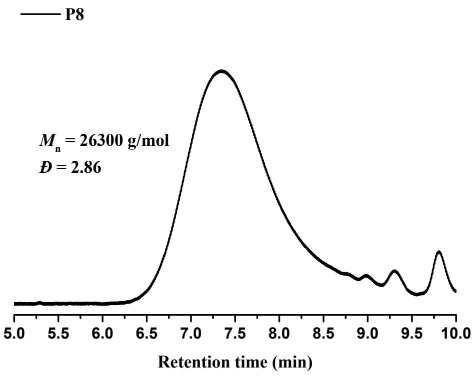


Figure S31. GPC traces of P8 in THF.

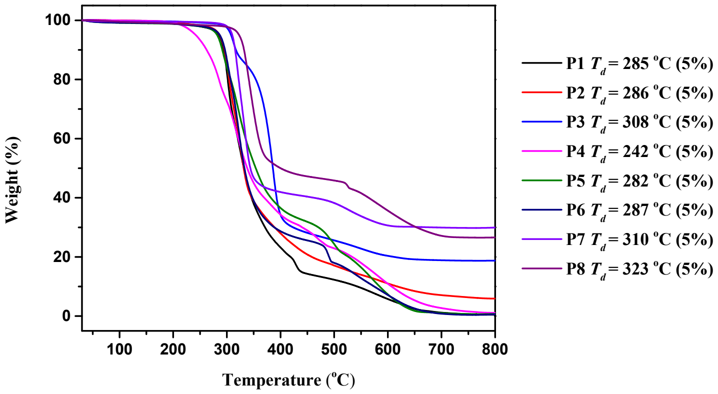


Figure S32. Thermogravimetic analysis of P1-8.

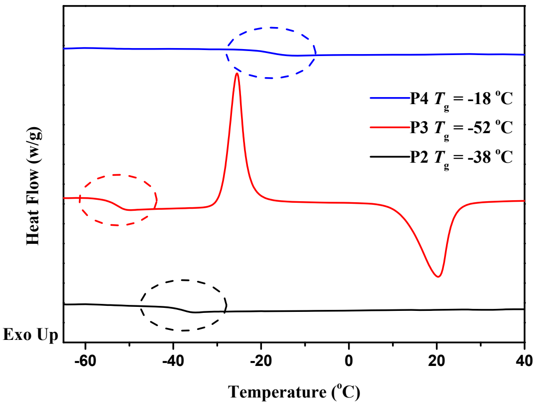


Figure S33. Differential scanning calorimeter of P2, P3 and P4.

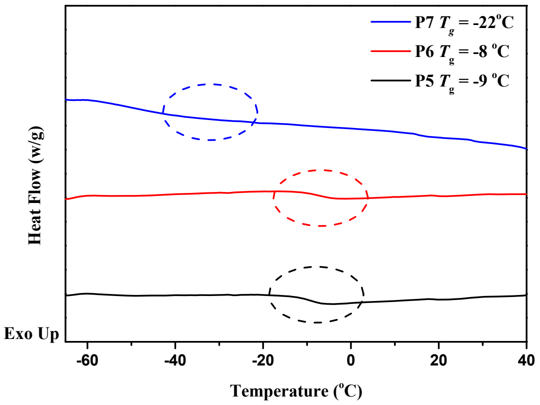


Figure S34. Differential scanning calorimeter of P5, P6 and P7.

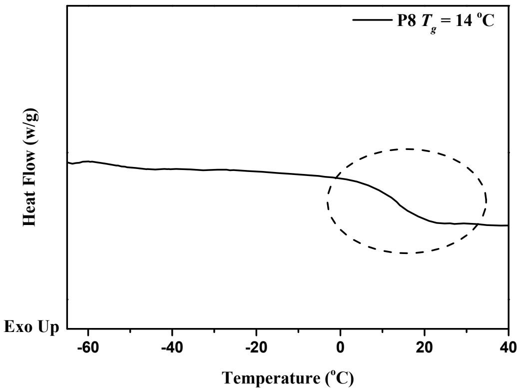


Figure S35. Differential scanning calorimeter of P8.

Table S1. Thermal analysis of Various selenide containing Polymers

Entry	M_n (g/mol)	TGA (5%)-T_d (°C)	DSC-T_g (°C)
P1	11000	285 °C	-41 °C
P2	10600	286 °C	-36 °C
P3	10200	308 °C	-54 °C
P4	4800	242 °C	-18 °C
P5	5600	282 °C	-9 °C
P6	5900	287 °C	-8 °C
P7	5400	310 °C	-22 °C
P8	26300	323 °C	14 °C

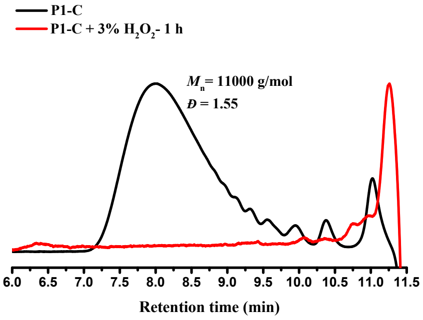


Figure S36. GPC curves of P1 before and after adding 3% H_2O_2.

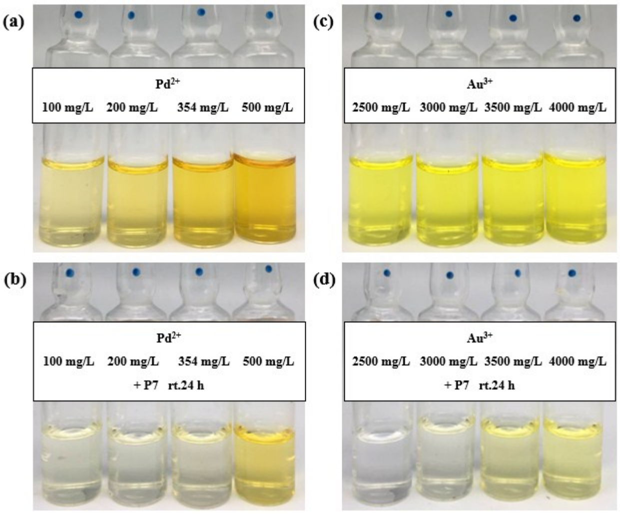


Figure S37. Adsorption of Pd^{2+} and Au^{3+} solutions by P7.

Table S2. Adsorption of Pd^{2+} solutions by P7

Entry	$[Pd^{2+}]_0$ mg/L	$[Pd^{2+}]$ mg/L	Efficiency (%)	Efficiency (mg /g)	Se/Pd^{2+} (mol/mol)
1	50	4.84	90	23	15.4
2	100	9.96	90	45	7.9
3	200	13.46	93	93	3.8
4 [a]	**354**	**35.8**	**90**	**159**	**2.23**
5	500	138.6	72	181	1.96

pH = 1.75, t = 24 h, m_{P7} = 10 mg [n (Se) = 0.0333 mmol.]

[a] 2n (Pd^{2+}) = n (Se).The mercury removal efficiencies of solid powder of P7 with 5 mL of Pd^{2+} solution. Palladium ion (Pd^{2+}) concentration was detected by ICP.

Table S3. Adsorption of Au^{3+} solutions by P7

Entry	$[Au^{3+}]_0$ mg/L	$[Au^{3+}]$ mg/L	Efficiency (%)	Efficiency (mg /g)	Se/Au^{3+} (mol/mol)
1	2000	10	>99	995	0.66
2	2500	29	99	1235	0.53
3	3000	43	99	1479	0.44
4	**3500**	**365**	**90**	**1617**	**0.41**
5	4000	776	81	1611	0.41

pH = 1.75, t = 24 h, m_{P7} = 10 mg [n (Se) = 0.0333 mmol.]
The mercury removal efficiencies of solid powder of P7 with 5 mL of Au^{3+} solution. Gold ion (Au^{3+}) concentration was detected by ICP.

References

1. Sashida, H.; Nakayama, A.; Kaname, M. *Synthesis* **2008**, 3229.