Electronic Supplementary Information (ESI)

Tailor-made chalcogen-rich polycarbonates: experimental and computational insights into chalcogen groups-dependent ring opening polymerization

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Part One. Experimental Details

Materials. All reagents were analytical-grade products, purchased from Sigma-Aldrich and Aladdin used as received unless otherwise noted. Dichloromethane (CH_2Cl_2) was dried with anhydrous magnesium sulfate ($MgSO_4$) for 48 h, followed by distillation. Anhydrous toluene was dried with sodium followed by distillation. 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), 1,5,7-triazabicyclo[4.4.0] dec-5-ene (TBD) and benzyl alcohol (BnOH) were distilled with CaH_2 under dry argon. The stock solution of BnOH was prepared in degassed CH_2Cl_2 at a final concentration of 0.5 mmoL/mL. Thiourea (TU) was prepared as previously reported.[1] The macrocarbonates (M_R) was synthesized by the intermolecular cyclization of functional diols and diphenyl carbonate through our previous method.[2]

Methods. NMR (^{1}H, ^{13}C) spectra were recorded on a Bruker Avance 400 spectrometer (400 MHz) and the data were analyzed with MestReNova software using deuterated chloroform ($CDCl_3$) and tetramethylsilane (TMS) as the internal standard. The molecular weights and molecular-weight distributions were obtained by gel permeation chromatograph (GPC) at 50 ^{o}C using DMF as the eluent at a flow rate of 1.0 mL min^{-1} and polymethyl methacrylate (PMMA) as the standard. Matrix-Assisted Laser Desorption/ Ionization Time of Flight Mass Spectrometry (MALDI-TOF-MS) was performed on an Applied Biosystems 4700 Proteomics Analyzer. Differential scanning calorimetry (DSC) was used to measure the glass transition temperatures (Tg) with a heating/cooling rate of 10 *°C*/min on DSC 204 F1 differential scan calorimeter (temperature range: – 70 to 100 °C). Thermal gravimetric analysis (TGA) was carried out on TGA/Pyris 1 TGA instrument with a heating rate of 10 *°C*/min from the room temperature to 600 °C under N_2 atmosphere.

The synthesis of macrocarbonates (MR)

The macrocarbonates (M_R) was synthesized by the intermolecular cyclization of functional diols and diphenyl carbonate through our previous method.[2] Briefly, funtional diols and diphenyl carbonate (150 mol % of functional diols) were dissolved in dried toluene (1/(500−600) g mL^{-1} concentration was appropriate to high yields). Then, lipase CA (100 wt % of enzyme to diphenyl carbonate) was added rapidly and the reaction was carried out at 70 ^{o}C for a determined time. After completing the reaction, lipase CA was removed by filtration and the solvent was evaporated under reduced pressure to obtain the crude products, which was washed with cold diethyl ether firstly. Then, the monomer was purified by recrystallized from ethyl acetate and n-hexane to result in crystalline solid. Alternatively, flash column chromatography using dichloromethane as the eluent can also be used to purify the macrocarbonates. The monomers were obtained with a yield of 35%-65%.

^{1}H NMR and ^{13}C NMR spectra were consistent with our previous literature[2] values.

General procedure for TBD catalytic ROP of macrocarbonates (MR)

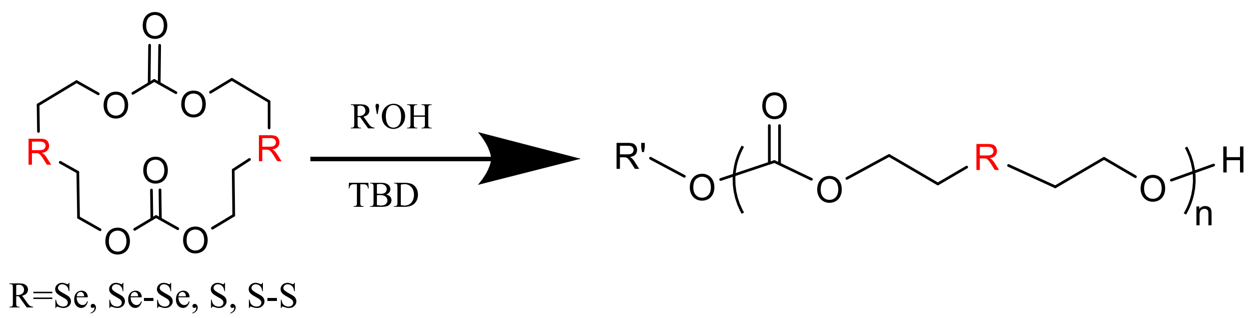
Representative ROP of MSe

In a 3 mL vial containing a stir bar, $\mathbf{M_{Se}}$ (98 mg, 0.25 mmol) and benzyl alcohol (25 µL, 0.0125 mmol) were added to a solution of TBD (1.75 mg, 1.25 mmol) in dry CH_2Cl_2 (0.2 mL). Then the other amount (CH_2Cl_2, 0.19 mL) was added to dissolve any remaining reactants fully at a determined monomer concentration of 0.64 M. The reaction mixture was stirred at room temperature. After 3 h, the reaction was quenched with acetic acid (~10 μL) and further was precipitated into anhydrous ether (~15 mL) to afford transparent viscous products (66 mg, 67% yield). The obtained polymers was characterized with NMR and GPC instrument.

Monomer conversion (~92%) was determined by comparing the area integral of the triplet at 4.46, corresponding to -CH_2SeCH_2- (8H) of monomer with that of the triplet at 4.36, corresponding to -CH_2SeCH_2- (8H) of polymer based on the following equation:

Monomer conversion (α)=m/(1+m)×100%

Where the area integral of the triplet at 4.46 (monomer) was normalized to 1, the area integral of the triplet at 4.36 (polymer) was m (See Figure S1).



Scheme S1. The TBD catalytic ROP of macrocarbonates with benzyl alcohol (BnOH) as the initiator in dichloromethane (CH_2Cl_2).

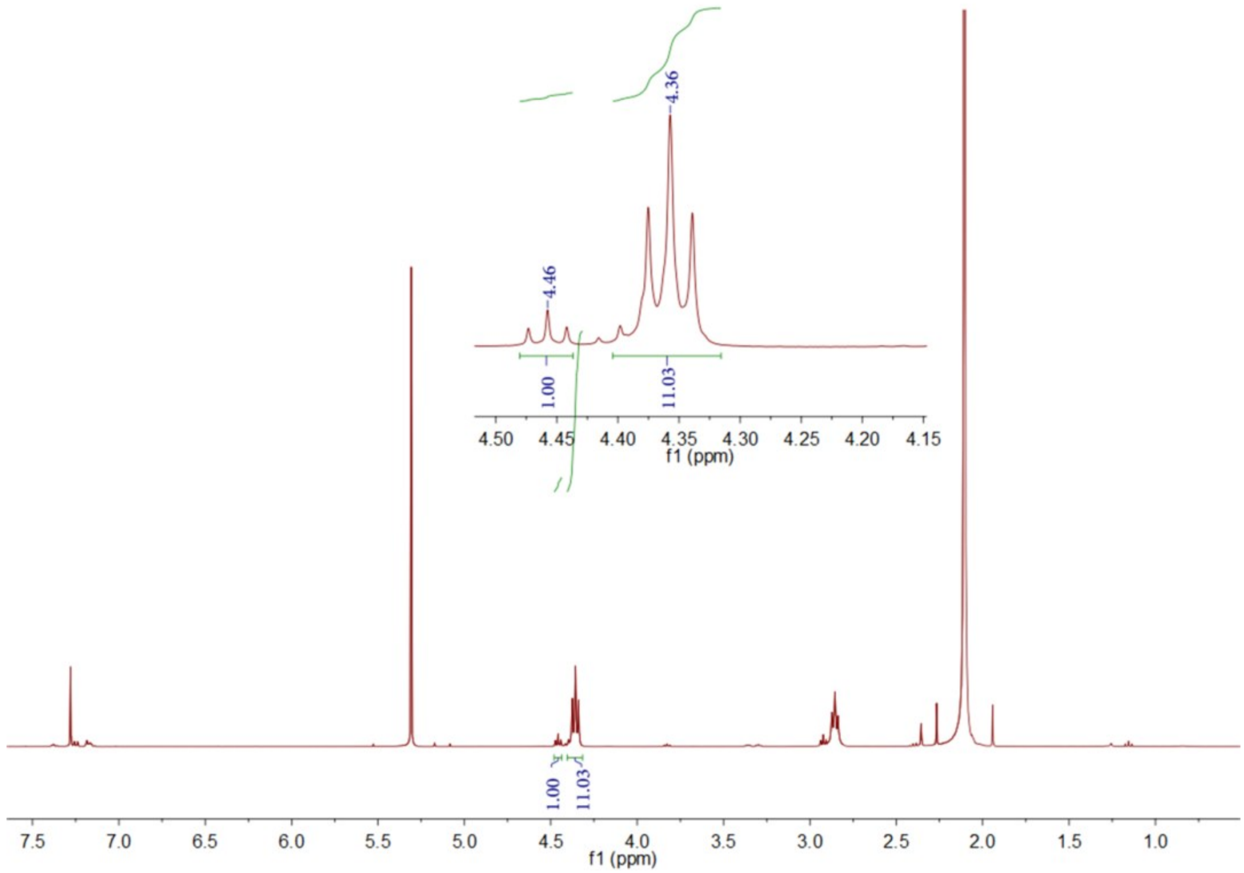


Figure S1. ^1H NMR spectrum for determining the monomer conversion of macrocarbonates (M_{Se}) in $CDCl_3$. When the area integral of the triplet at 4.46 (monomer) was normalized to 1, the conversion was calculated as α = 11.03

/ (11.03+1) = ~92%.

General polymerization kinetics experiment

The TBD catalytic ROP kinetics experiment was carried out using M_{Se} as an example: In a J-Young NMR tube, M_{Se} (100 mg, 0.256 mmol) and benzyl alcohol (25 μL, 0.0125 mmol) were added to a solution of TBD (1.75 mg, 1.25 mmol) in dry CH_2Cl_2 (0.2 mL). Then an anothor amount (CH_2Cl_2, 0.2 mL) was added to dissolve any remaining reactants fully at a determined monomer concentration of 0.64 M. Then, the J-Young tube was taken to an Bruker Avance 600 spectrometer and the date was recorded at a determined time intervals.

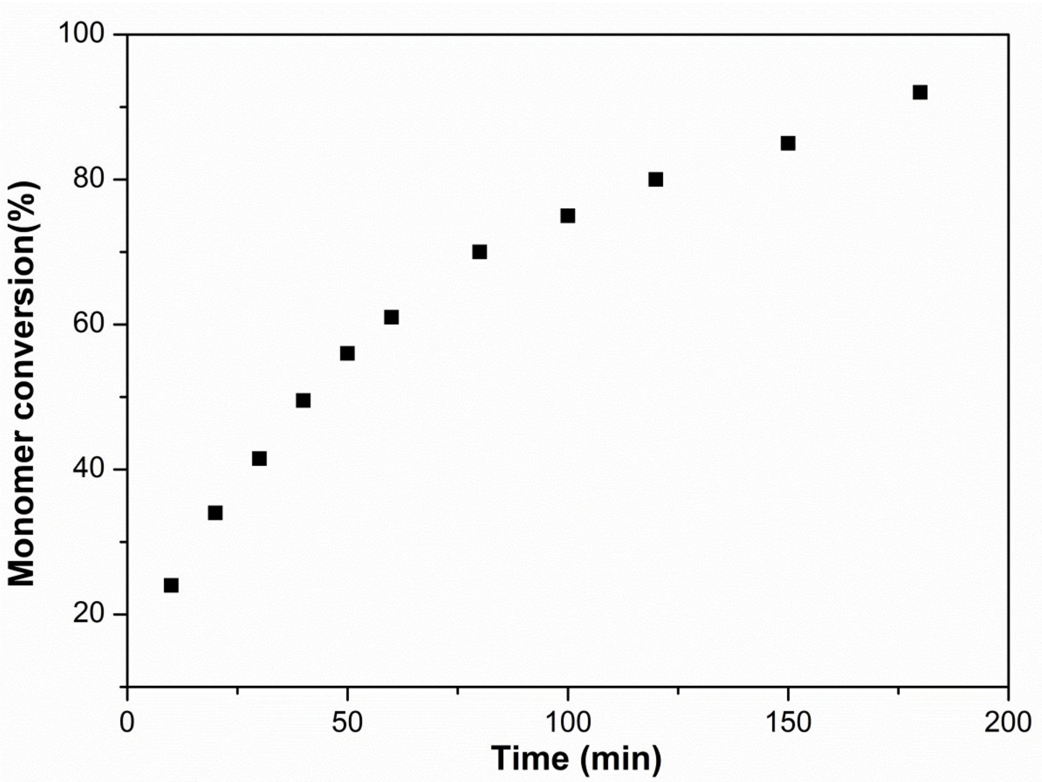


Figure S2 The monomer M_{Se} conversion vs reaction time determined by ^{1}H NMR in CD_2Cl_2.

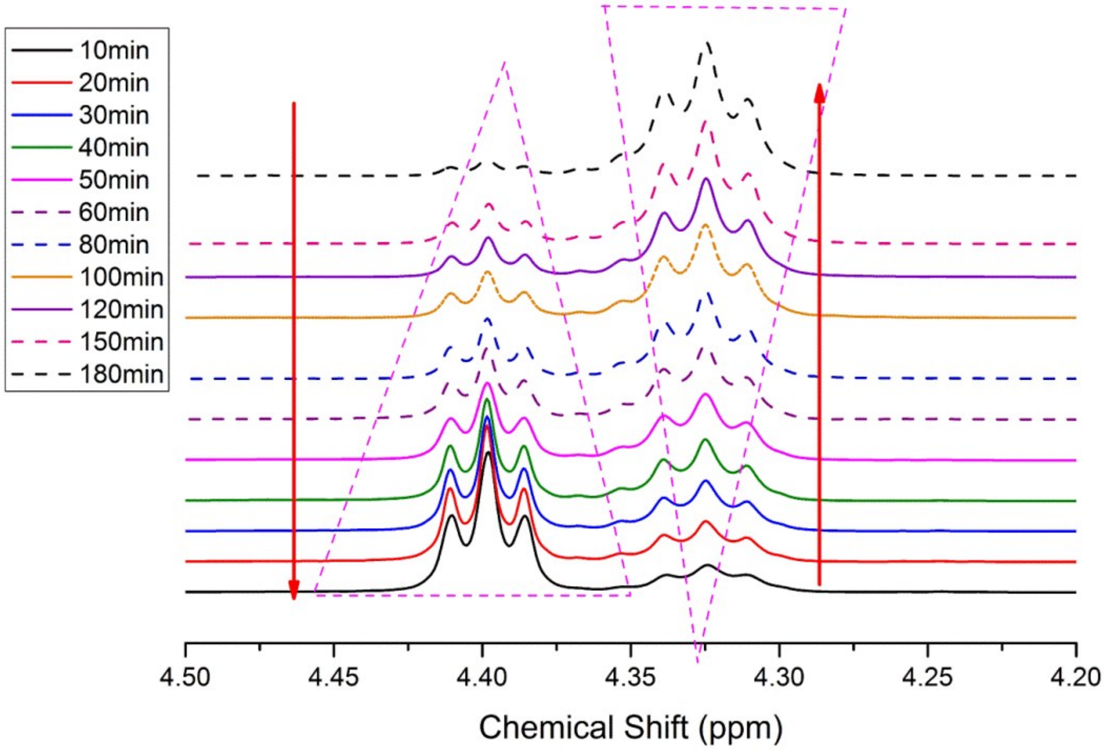


Figure S3 ^{1}H NMR spectrum detection of TBD catalytic ROP of macrocarbonates (M_{Se}) inCD_2Cl_2.

Chain extension experiment

In a 3 mL vial containing a stir bar, M_{Se} (49 mg, 0.125 mmol) and benzyl alcohol (25 µL, 0.0125 mmol) were added to a solution of TBD (0.9 mg, 0.65 mmol) in dry CH_2Cl_2 (0.1 mL). Then the other amount (CH_2Cl_2, 0.1 mL) was added to stirred at room temperature for 3 h. Then, 20 µL solution was taken out for ^{1} H NMR and GPC analysis. Subsequently, second portion of 10 equiv. M_{Se} (49 mg, 0.125 mmol) in 0.2 mL CH_2Cl_2 was added to react for another 6 h. 20 µL solution was also taken out for ^{1} H NMR and GPC analysis.

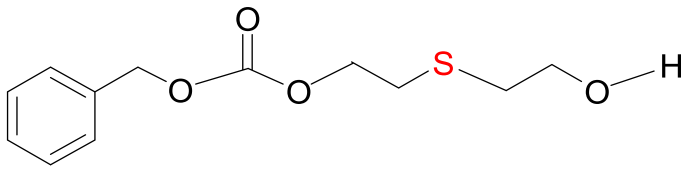
Mechanism study by 1H NMR spectra

1:1 Mixtures of organocatalyst with Benzyl Alcohol：5 mg (0.036 mmol) TBD in 0.6 mL D_2Cl_2 and 3.88 mg (0.036 mmol) BnOH in 0.6 mL D_2Cl_2 were analyzed by ^{1}H NMR, respectively. Then, the above TBD and BnOH solution was mixed to perform ^{1}H NMR analysis.

1:1 Mixtures of organocatalyst with monomer：5 mg (0.036 mmol) TBD in 0.6 mL D_2Cl_2 and 14 mg (0.036 mmol) M_{Se} in 0.6 mL D_2Cl_2 were analyzed by ^{1}H NMR, respectively. Then, the above TBD and M_{Se} solution was mixed to perform ^{1}H NMR analysis.

Supporting NMR and GPC data of polymers

PS (Designed DP=20)



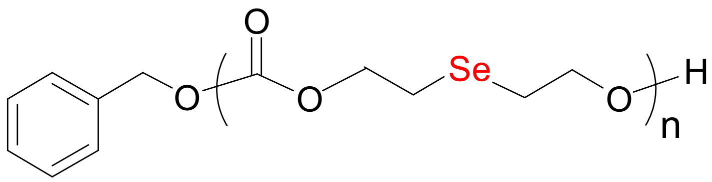
^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 4.30 (t, 8H), 2.84 (t, 8H);

^{13}C NMR (400 MHz, $CDCl_3$, δ, ppm): 154.7, 66.8, 30.6;

M_n (^{1}H NMR) = 6.0 kg/mol (DP=20);

M_n (GPC) = 9.6 kg/mol $Đ_M$=1.31;

PSe (Designed DP=20)



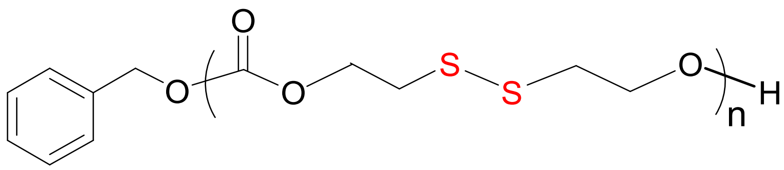
^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 4.35 (t, 8 H), 2.85 (t, 8H);

^{13}C NMR (400 MHz, $CDCl_3$, δ, ppm): 154.6, 67.5, 21.8;

M_n (^{1}H NMR) = 7.5 kg/mol (DP=19);

M_n (GPC) = 9.5 kg/mol $Đ_M$=1.30;

PSS (Designed DP=20)



^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 4.41 (t, 8 H), 2.98 (t, 8H);

^{13}C NMR (400 MHz, $CDCl_3$, δ, ppm): 154.7, 65.8, 37.0;

M_n (^{1}H NMR) = 6.9 kg/mol (DP=19);

M_n (GPC) = 9.8 kg/mol $Đ_M$=1.29;

PSeSe (Designed DP=20)

The monomer conversion was low (<35% determined by ^{1}H NMR) and the GPC showed very low molecular weight (hundreds) (See Figure S4 and Figure S5).

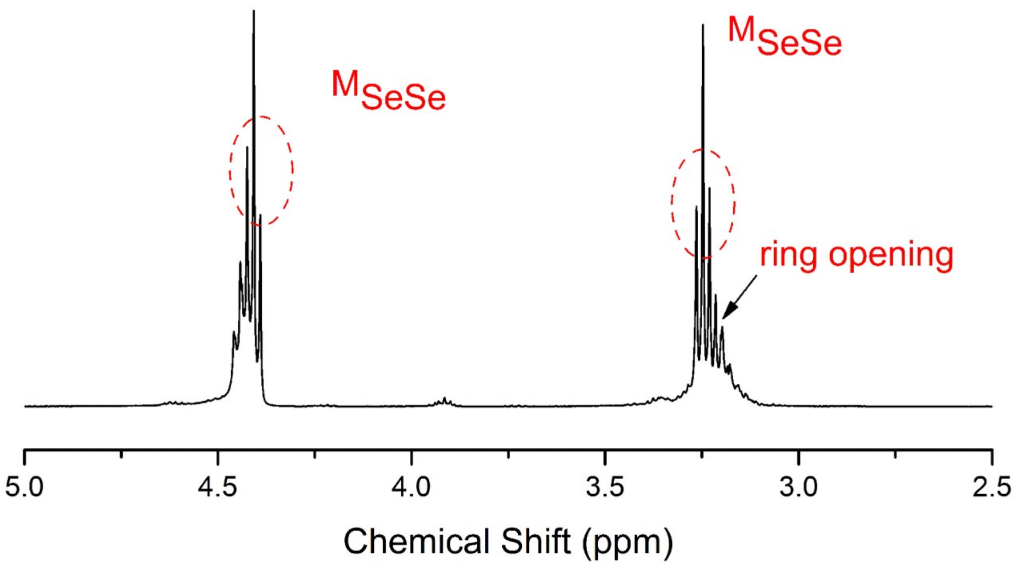
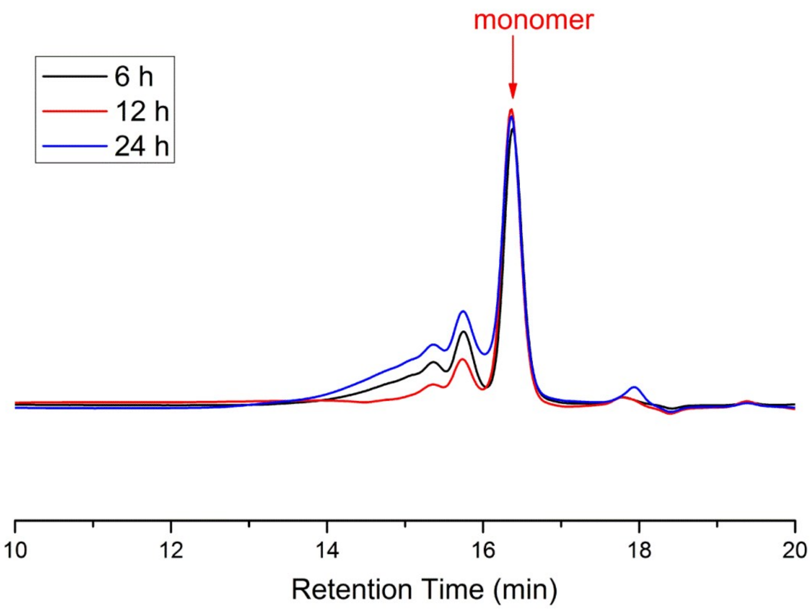


Figure S4 [1]H NMR spectrum of the polymerization product of M_{SeSe} in $CDCl_3$ without purification. The monomer conversion was low (~31%).



FigureS5 GPC curves of the polymerization product of M_{SeSe} without purification showed still existing a lot of monomers and a small number of low molecular weight oligomers (hundreds). The results indicated that ROP of M_{SeSe} underwent quite slow ring opening and chain propagation, which could be responsible for the large steric hindrance derived from four selenium atoms.

Results of TBD, DBU, TU organocatalytic ROP of macrocarbonates

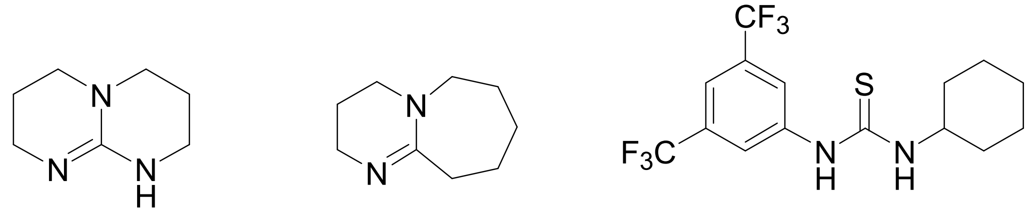


Table S1. Results of ROP of macrocarbonates using different organocatalysts[a].

Entry	Cat. (C)	macrocarbonates	[M]/[I]/[C][b]	Time/h	Conv. (%)[c]
1	TBD	M_S	20:1:1	2	97
2	TBD	M_{Se}	20:1:1	3	92
3	TBD	M_{SS}	20:1:1	3	85
4	TBD	M_{SeSe}	20:1:1	24	31
5	DBU	M_S	20:1:1	24	0
6	DBU[d]	M_S	20:1:1	24	0
7	DBU	M_{Se}	20:1:1	24	0
8	DBU	M_{SS}	20:1:1	24	0
9	DBU	M_{SeSe}	20:1:1	24	0

[a] All reactions were conducted with benzyl alcohol as the initiator at the specified initial monomer concentration $[M]_0$=0.64 M at 25 °C in CH_2Cl_2. [b] [Monomer]:[ROH]:[catalyst]. [c] M_n (kDa) determined by ^{1}H NMR spectroscopy.[d]5 mol % TU added relative to monomer.

Table S2. TBD catalytic ROP of M_{Se} at different conditions in CH_2Cl_2**.**

Entry[a]	Initiator	Monomer	[M]	[M]/[I]/[C][b]	T/h	conv. (%)[c]	M_n[c]	M_n[d]	M_n[e]	PDI[e]
1	Bn-OH	M_{Se}	0.32	20:1:1	3	83	7900	7000	13900	1.26
2	Bn-OH	M_{Se}	0.64	20:1:1	3	92	7900	7100	14600	1.30
3	Bn-OH	M_{Se}	0.96	20:1:1	1	93	7900	7600	17000	1.30
4	Bn-OH	M_{Se}	1.28	20:1:1	1	97	7900	7900	13800	1.44
5	Bn-OH	M_{Se}	0.96	20:1:0.2	6	61	7900	4200	12000	1.28
6	Bn-OH	M_{Se}	0.96	20:1:0.1	6	32	7900	2200	8500	1.18
7	mPEG-OH	M_{Se}	0.64	10:1:0.5	3	94	5900	5900	15100	1.25
8	mPEG-OH	M_{Se}	0.64	20:1:1	3	87	9800	9100	23000	1.30
9	mPEG-OH	M_{Se}	0.96	20:1:1	2	97	9800	9800	16800	1.31

[a] All reactions were conducted in CH_2Cl_2 using TBD as catalysts. [b] The mol ratio of monomer to initiator and catalyst.[c] Molecular weight calculated by the feed ratios. [d] As determined by ^{1}H NMR spectroscopy. [e] As determined by GPC.

Thermal properties of poly (chalcogen-carbonate)s

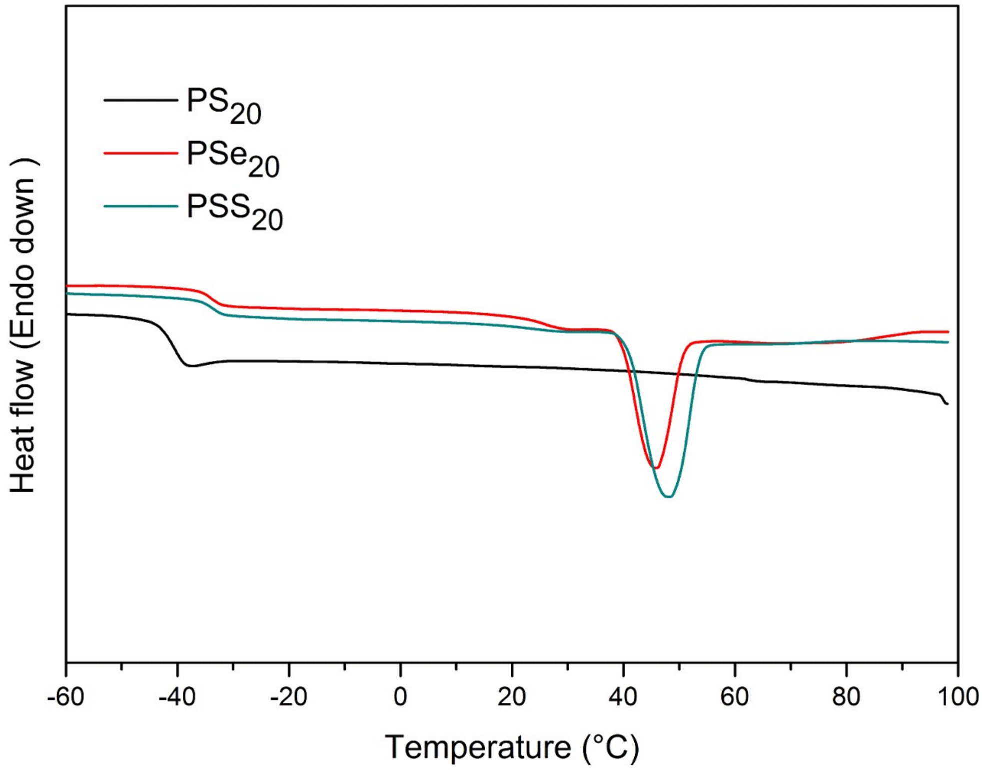


Figure S6 Overlay of the DSC curves of different poly (chalcogen-carbonate)s (PS_{20}[3], PSe_{20}, entry 9 Table 1 and PSS_{20}, entry 13 Table 1).

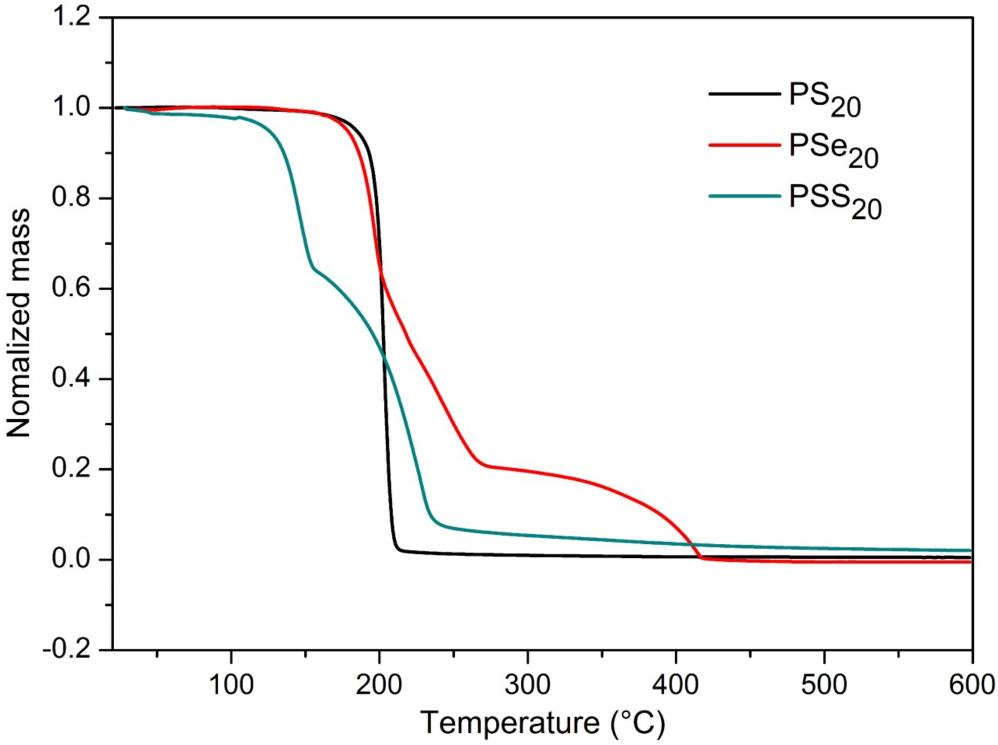


Figure S7 Overlay of the TGA curves of different poly (chalcogen-carbonate)s ((PS_{20}[3] , PSe_{20} entry 9 Table 1 and PSS_{20}, entry 13 Table 1)). The broader and two-time mass loss is likely a consequence of the degradation of functional groups.

Table S3 Summary of the thermal properties of different poly (chalcogen-carbonate)s.

	PS_{20}[3]	PSe_{20}	PSS_{20}
T_g (°C)[a]	-41.6	-34.1	-33.9
T_m (°C)[a]	\	45	48
T_{onset} (°C)[b]	180	175	121
T_d(°C)[b]	218	202	195

[a]Tg: glass transition temperature, determined by DSC. [b] T_{onset} (°C)*: started* loss decomposition temperature [b]Td: 50% weight loss decomposition temperature, determined by TGA.

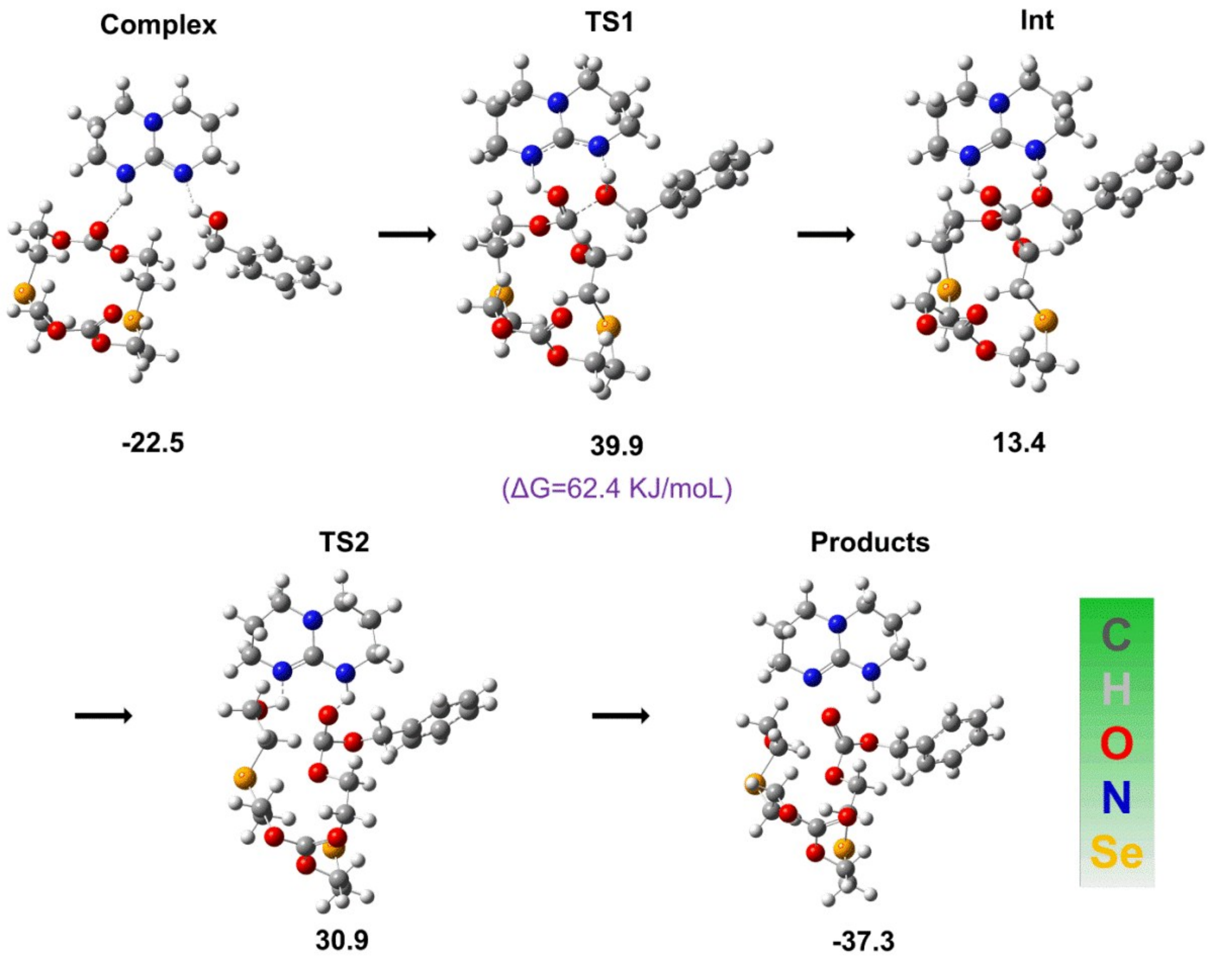
Part two. Computational Details:

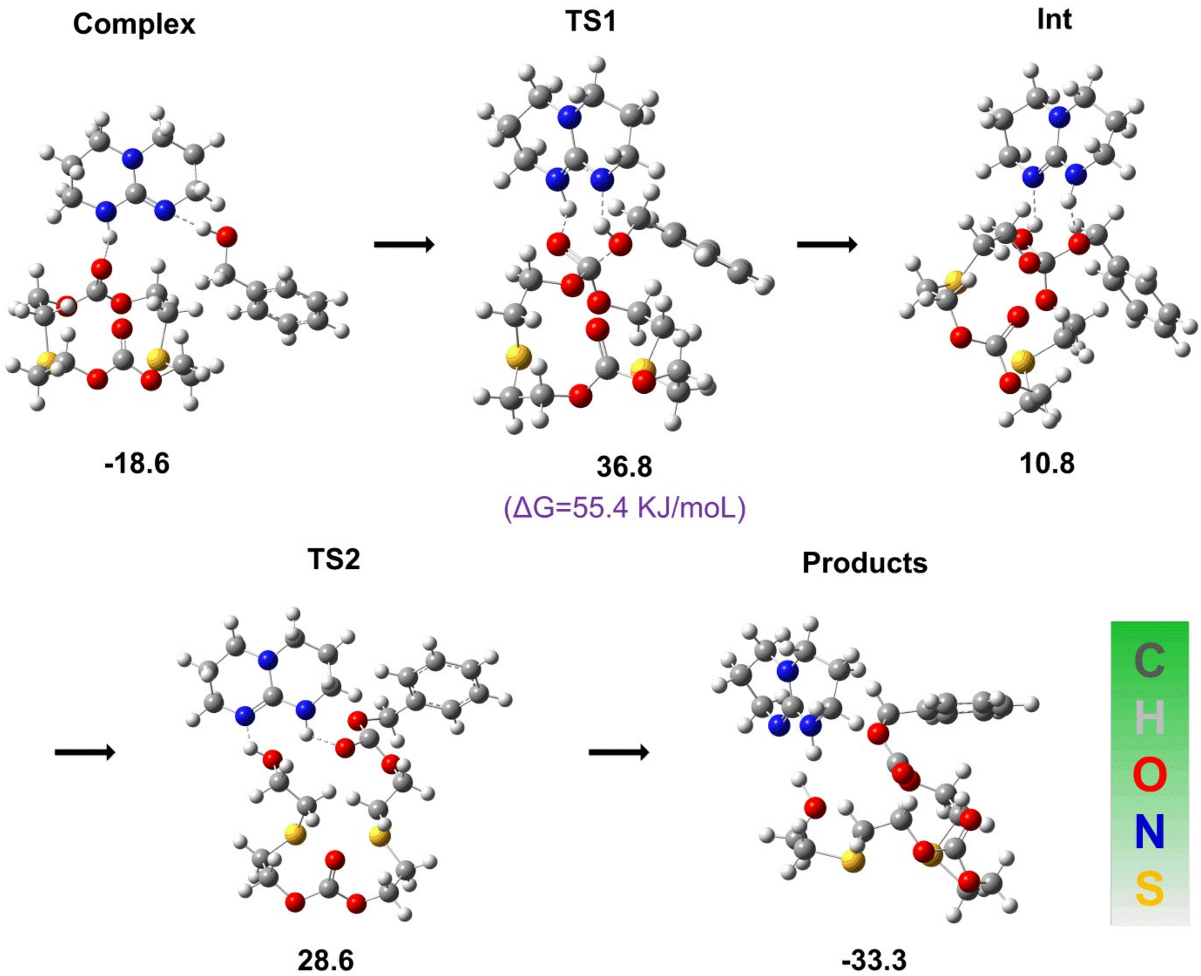
Computational Details

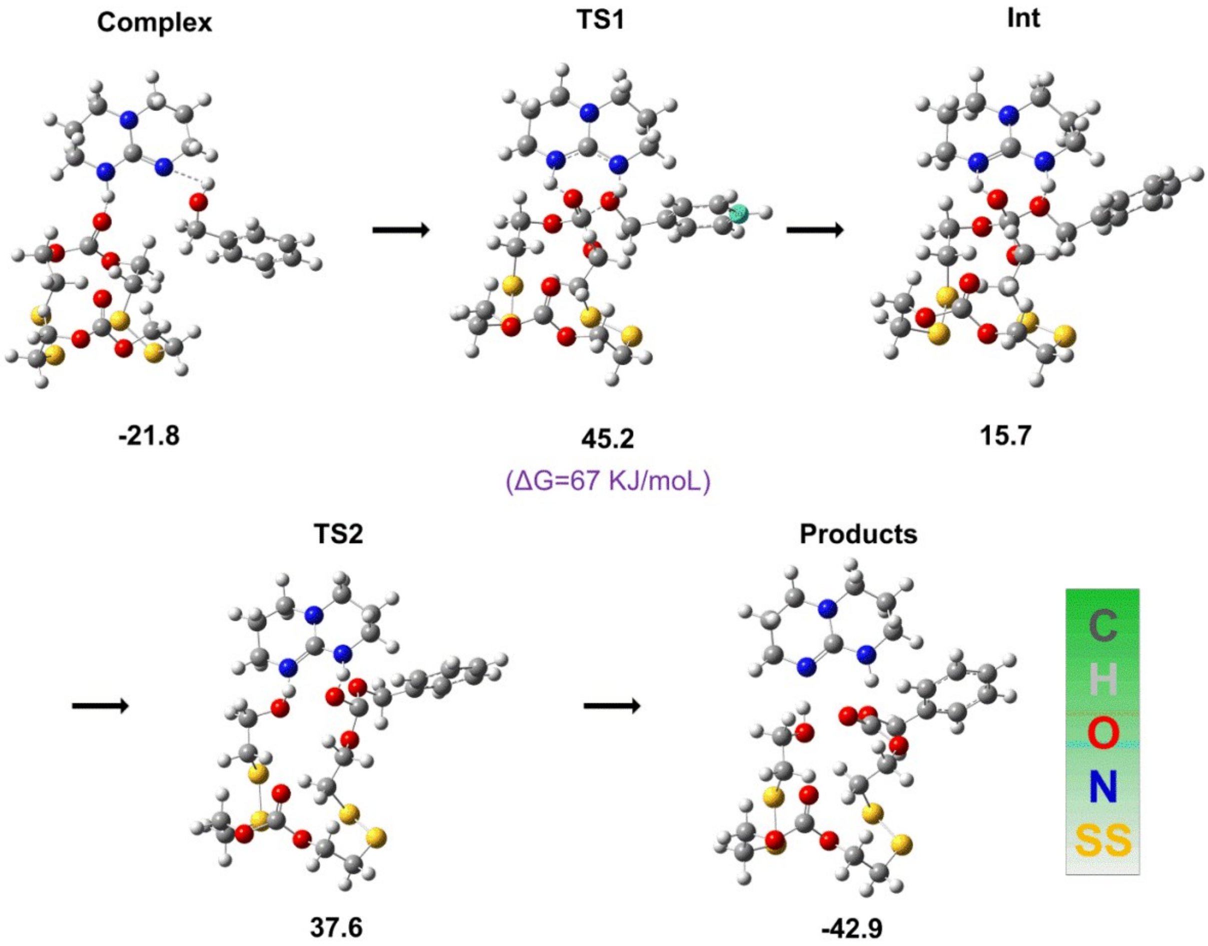
All the density functional calculations (DFT) have been carried out with the Gaussian 09 suite of programs by using the B3LYP functionals[4]. Geometry optimizations were performed in the presence of dichloromethane which modeled by the by continuum dielectric (c-PCM) method[5] with default parameters(ε=8.93) using the 6-31+G(d) basis set. All calculations were performed with the overall molecular charges being zero and singlet ground state multiplicities.

These frequencies were then used to evaluate the zero-point vibrational energy (ZPVE) and the thermal corrections, at T = 298 K, to the enthalpy and Gibbs free energy in the harmonic oscillator approximation. The electronic energy was refined by single-point calculations using the 6-311++G(d,p) basis set[6]

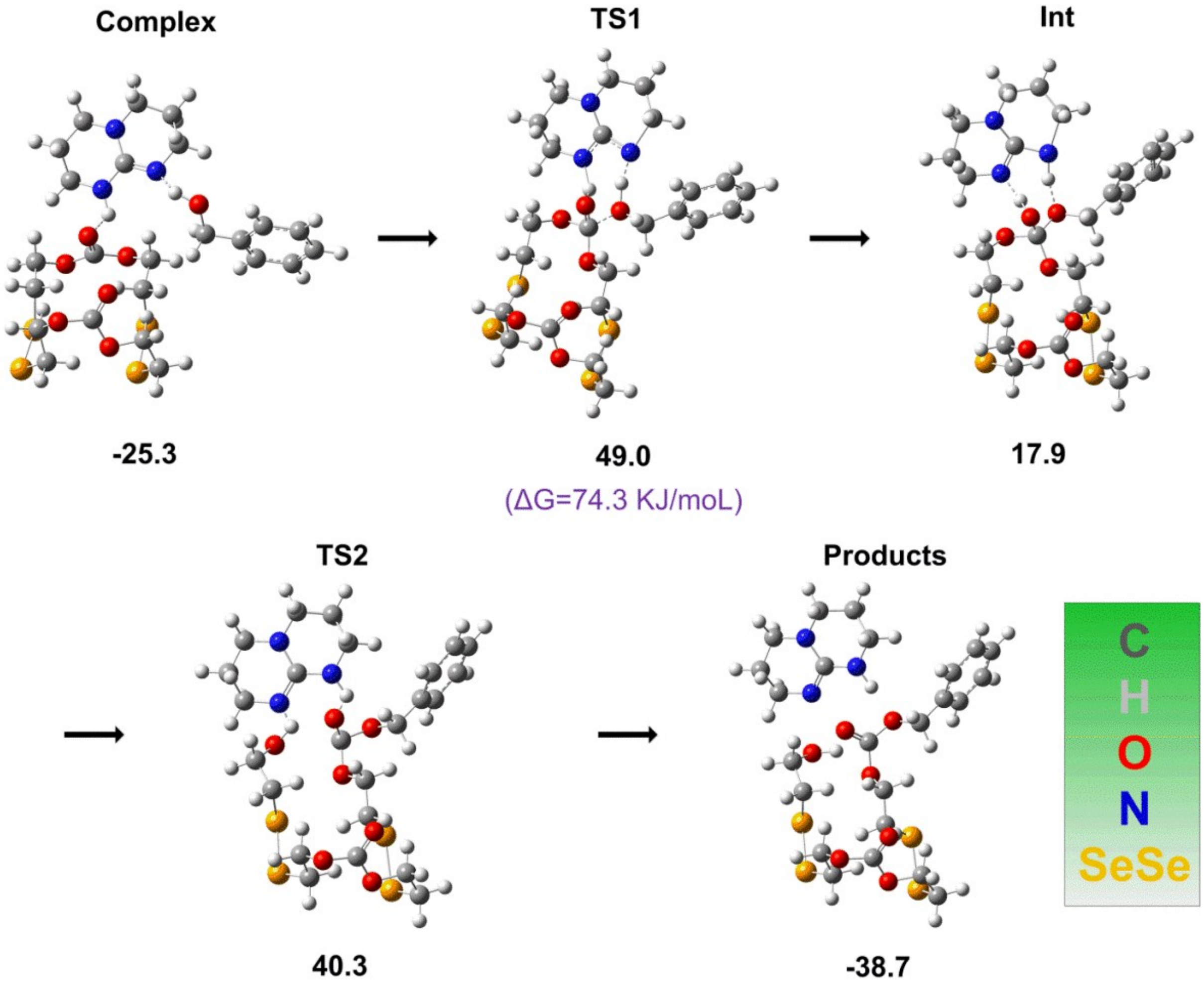
The proposed mechanism for TBD catalytic ROP of M_R and the free energies and optimized structures of intermediate states of M_R




Complex
TS1
Int
-18.6
36.8
(ΔG=55.4 KJ/moL)
10.8
TS2
Products
28.6
-33.3
C
H
O
N
S

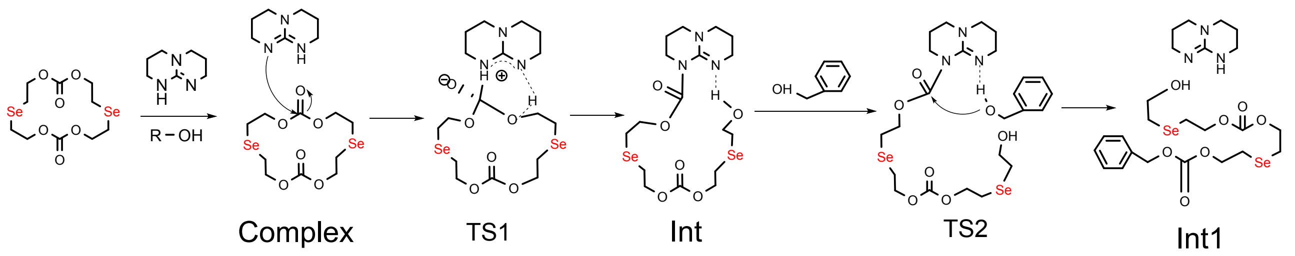


Complex
TS1
Int
-21.8
45.2
(ΔG=67 KJ/moL)
15.7
TS2
Products
37.6
-42.9
C
H
O
N
SS

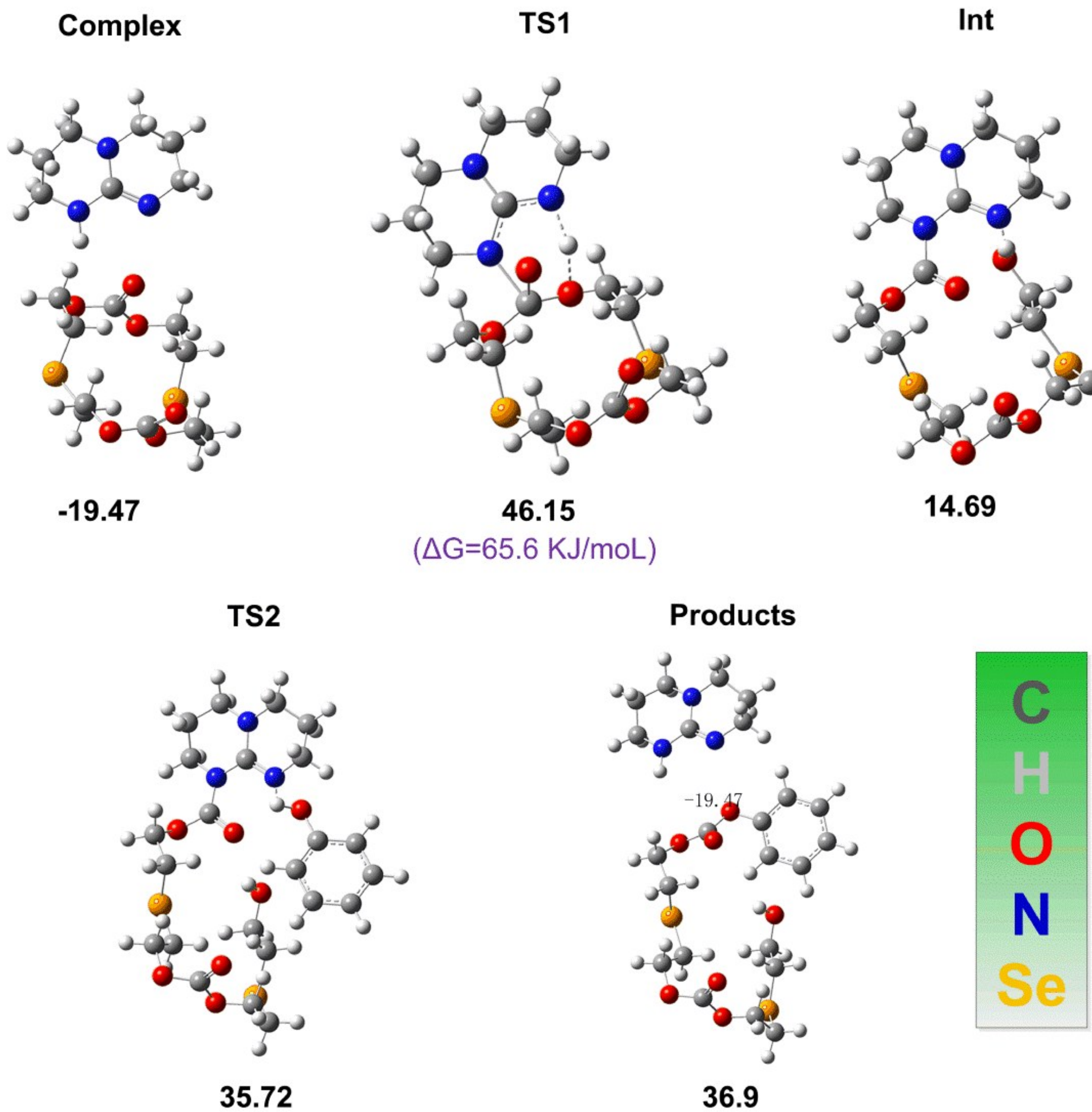


Complex
TS1
Int
-25.3
49.0
(ΔG=74.3 KJ/moL)
17.9
TS2
Products
40.3
-38.7
C
H
O
N
SeSe

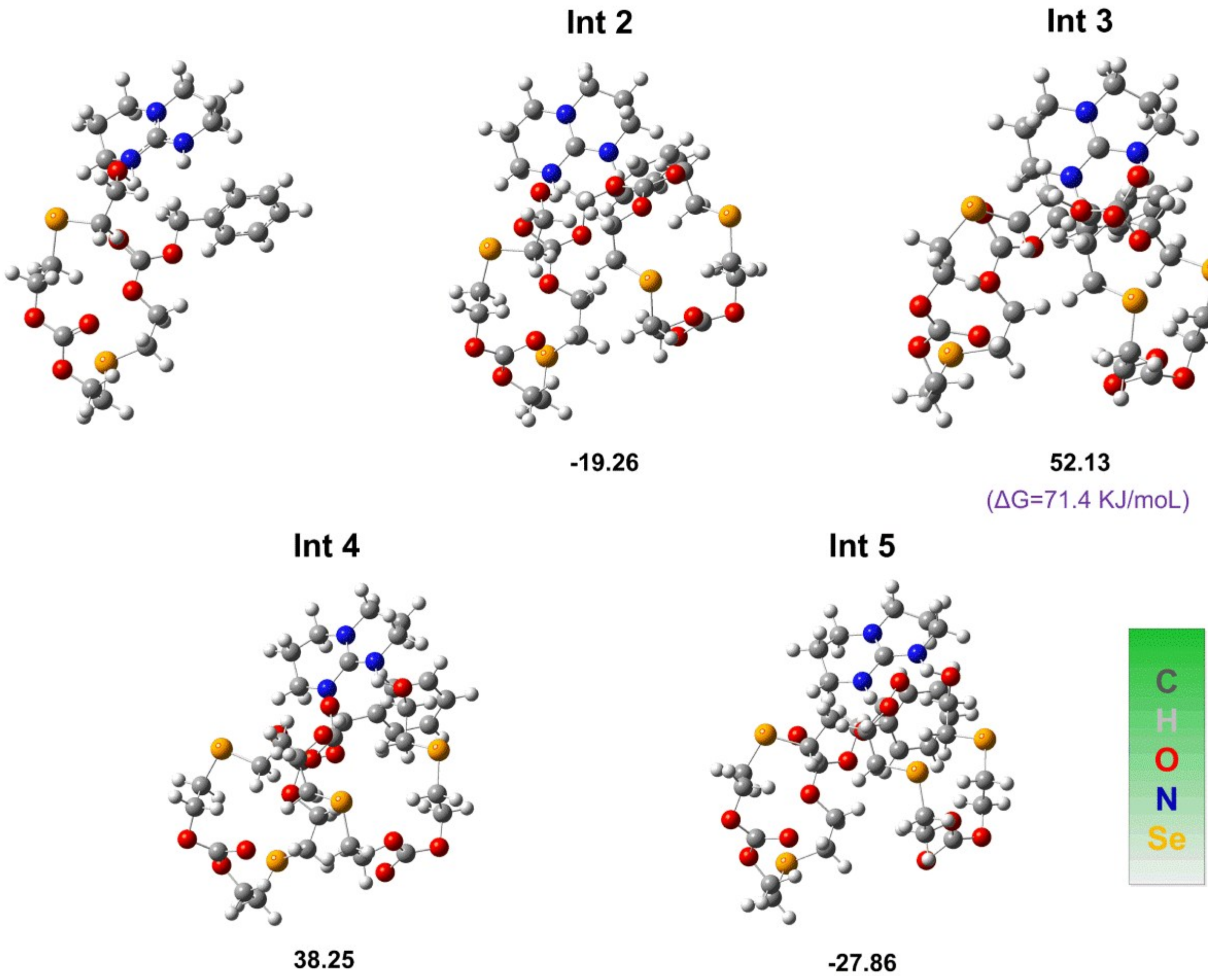
An alternative mechanistic pathway through dual activation of monomer and initiator by TBD

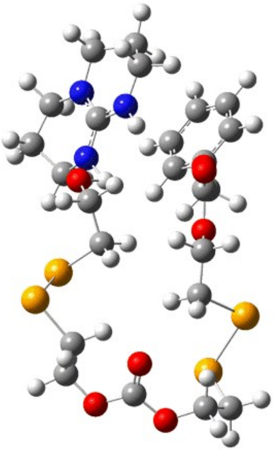


Scheme S2 An alternative mechanistic pathways through dual activation of monomer and initiator by TBD, involving direct covalent bonding by which TBD inserts into the carbonate bond, and subsequently an incoming initiator attacks the intermediate to form polycarbonates.

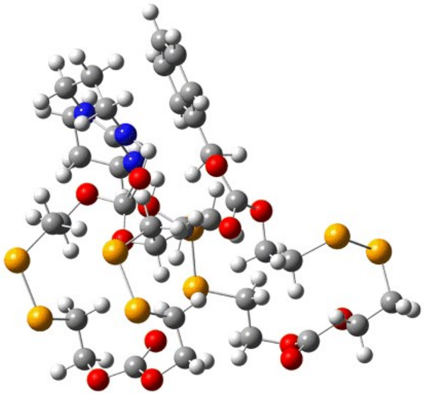


Chain growth of M_{Se} and M_{SeSe}



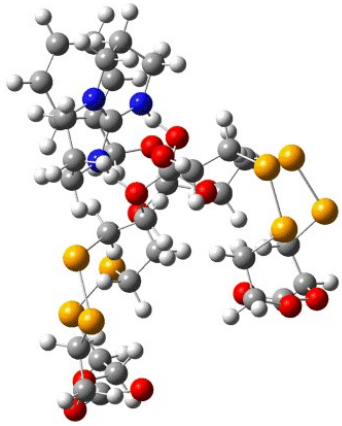


Int 2



-28.73

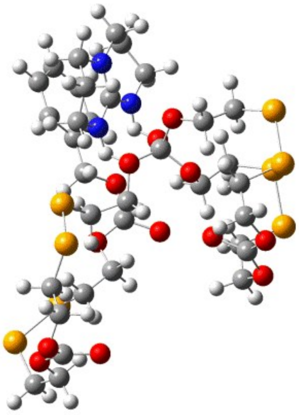
Int 3



67.28

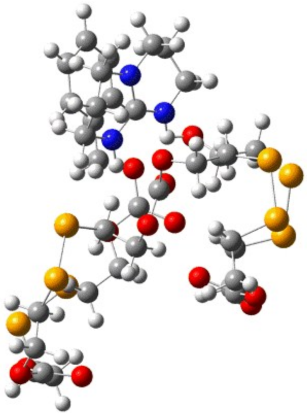
(ΔG=96.0 KJ/moL)

Int 4

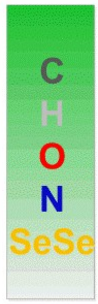


45.67

Int 5



-29.54



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Copies of NMR and GPC Spectra for Polymers

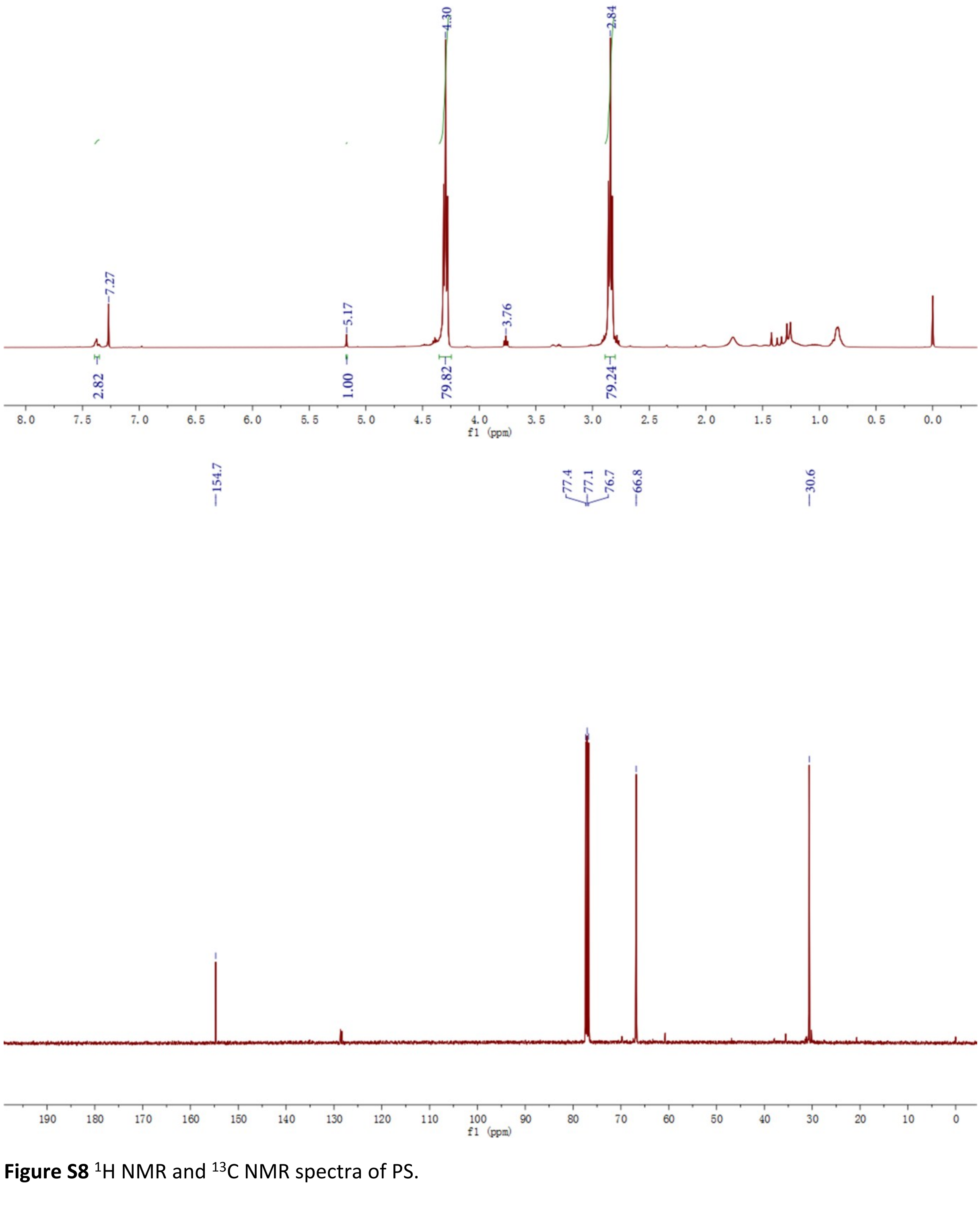
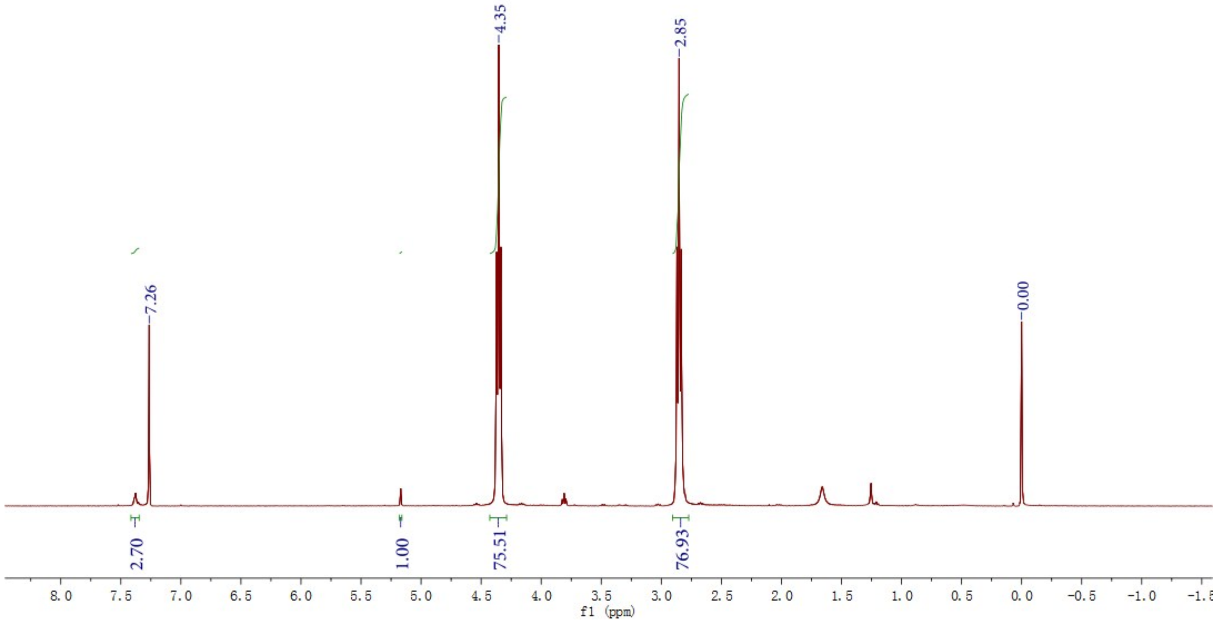


Figure S8 ^{1}H NMR and ^{13}C NMR spectra of PS.



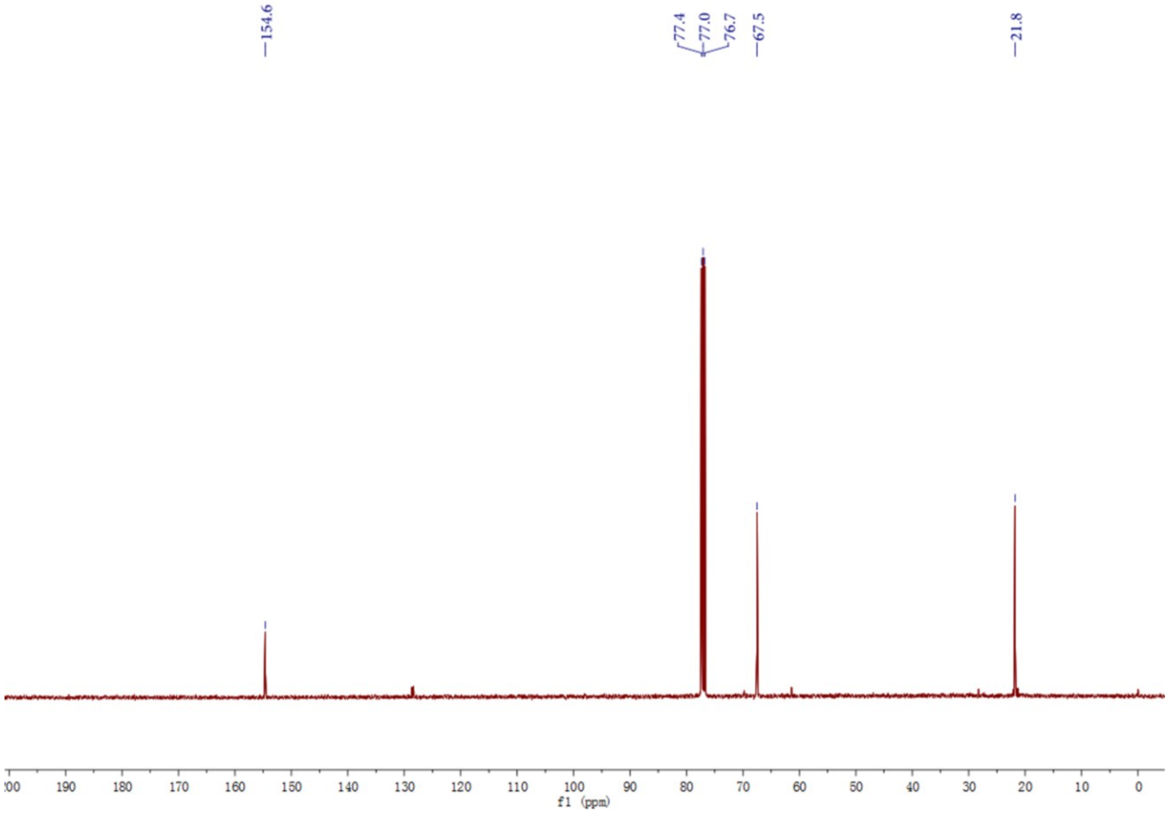
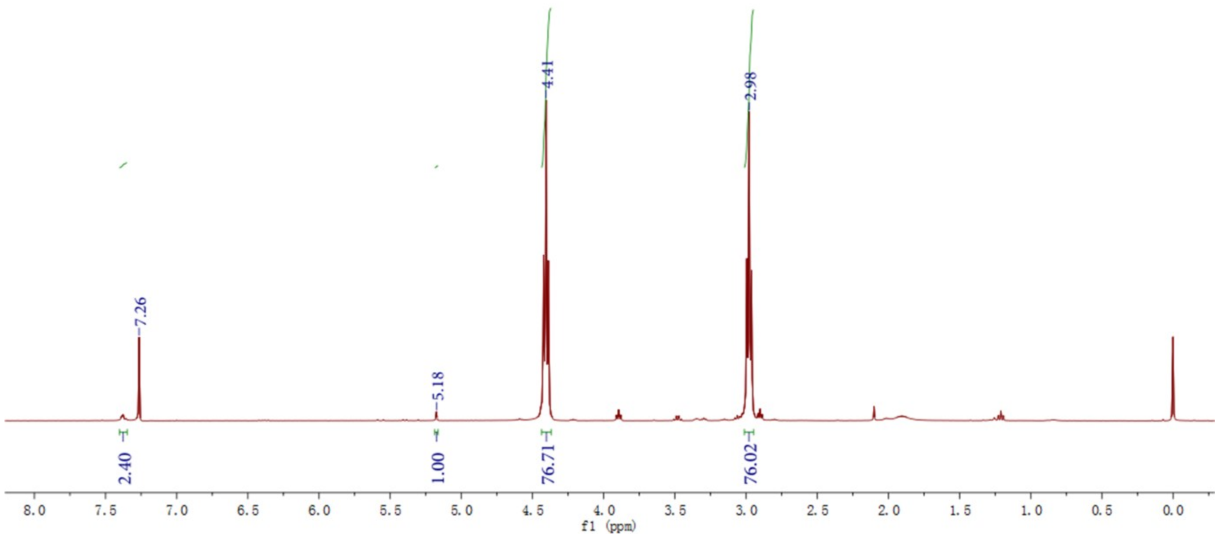


Figure S9 ^{1}H NMR and ^{13}C NMR spectra of PSe.



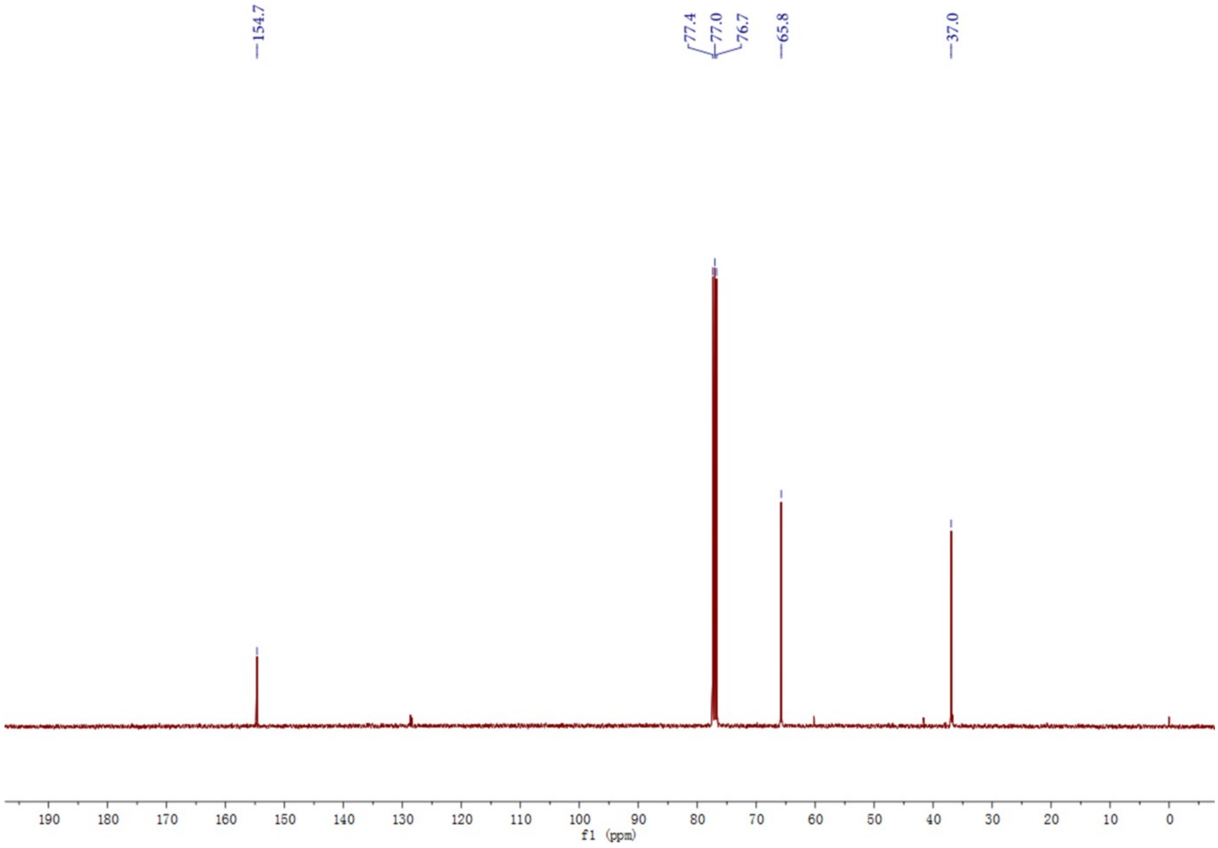


Figure S10 ^{1}H NMR and ^{13}C NMR spectra of PSS.

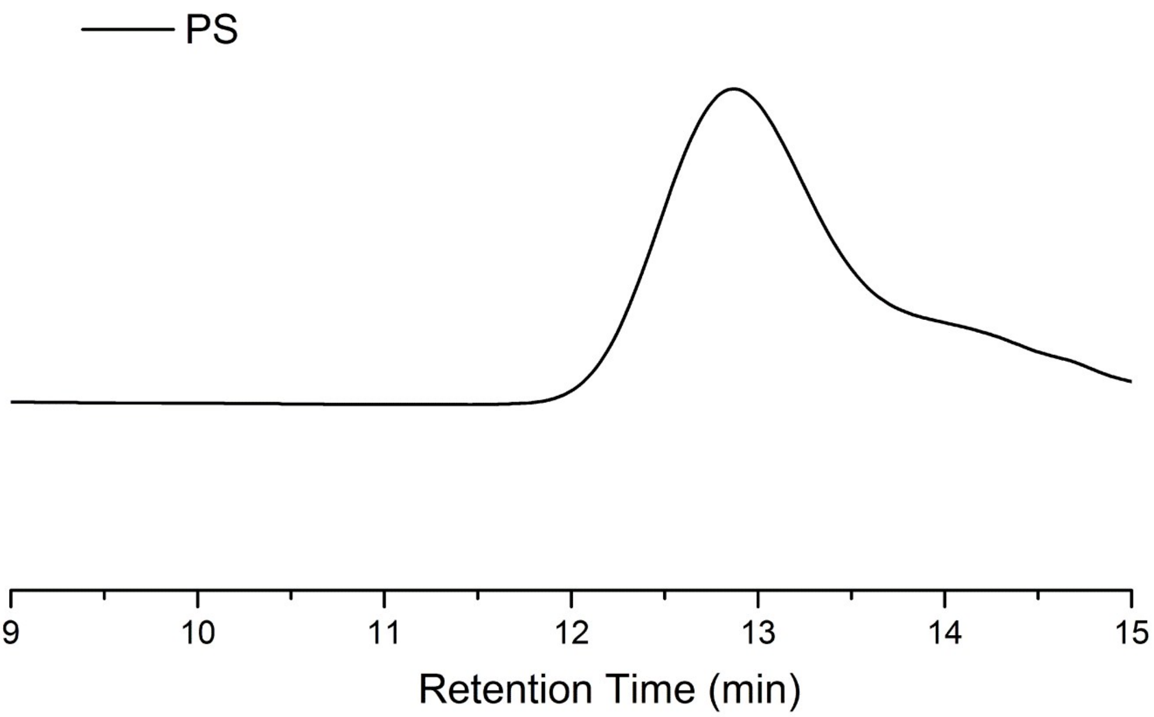


Figure S11 GPC chromatograph of polymer PS .

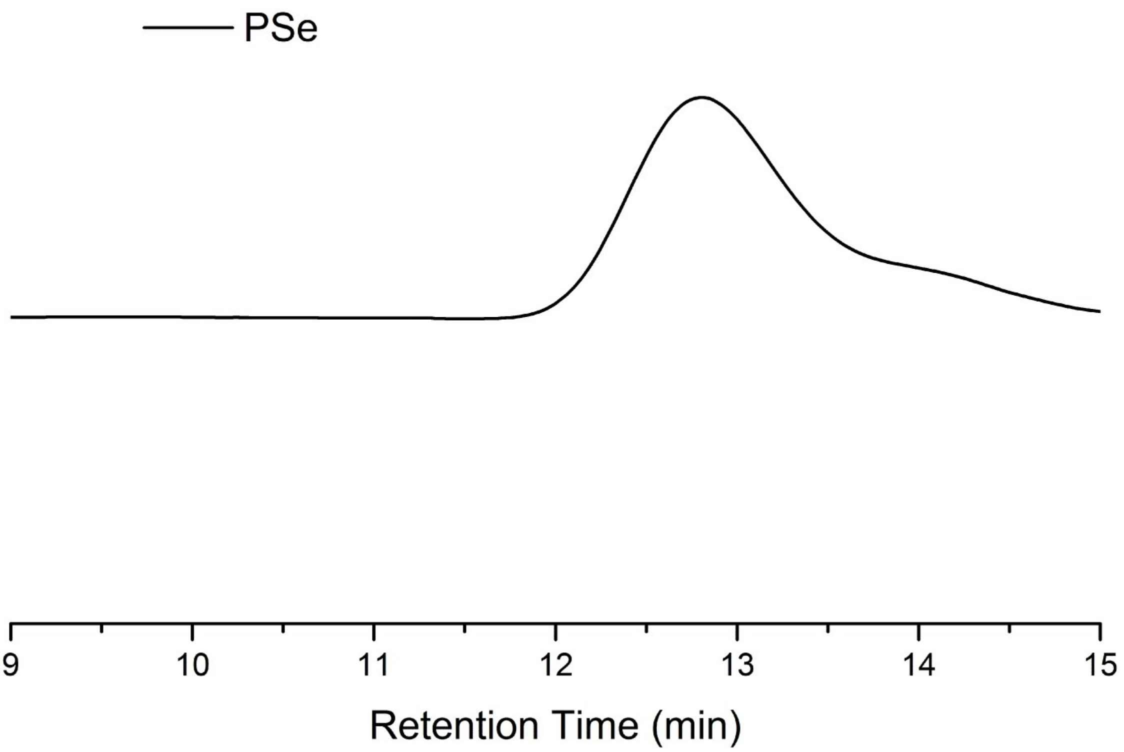


Figure S12 GPC chromatograph of polymer PSe.

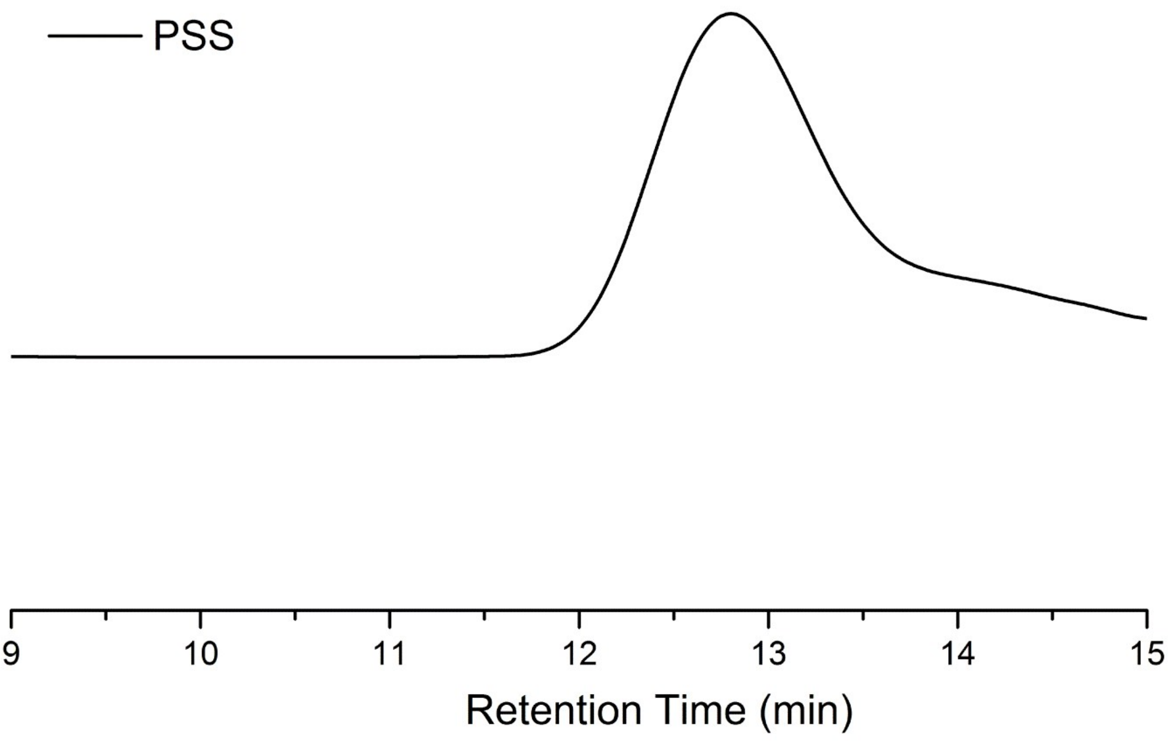


Figure S13 GPC chromatograph of polymer PSS.