Supporting Information

Stereoregular poly(2-phenylthiirane) *via* cationic ring-opening polymerization

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Contents

1. General information

All chemicals and reagents were purchased from commercial sources and were further no purified before used. Besides, PPN = bis(triphenylphosphine)iminium ([PPN]Cl) was purified by recrystallization from dichloromethane (DCM)–diethyl ether. The 2-phenylthiirane was dried using CaH_2 and distilled before use. All manipulations involving air-sensitive and water-sensitive compounds were carried out in a glovebox or with the standard Schlenk techniques under dry argon. All solvents used in the reactions like DCM, toluene and tetrahydrofuran (THF) were dried over 3 Å under nitrogen before use.

Nuclear Magnetic Resonance (NMR): ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker Varian INOVA-400 MHz type (^{1}H NMR, 400 MHz; ^{13}C NMR, 100 MHz) spectrometer in deuterated. Their peak frequencies were referenced versus an internal standard TMS shifts at 0.00 ppm for ^{1}H NMR and against the solvent $CDCl_3$ at 77.16 ppm for ^{13}C NMR, respectively.

Gel permeation chromatography (GPC): Molecular weights and molecular weight distributions of polymers were measured by GPC analysis at 30 °C and a flow rate of 1.0 mL/min, with THF as the eluent and polystyrene as the standards, on an Agilent 1260 instrument coupled with an Agilent RI detector and equipped with two PL gel columns. The sample concentration was about 1 mg/mL, and the injection volume was 100 μL.

Differential scanning calorimetry (DSC): The analysis of DSC was carried out with a Mettler-Toledo DSC 3 thermal analyzer. Conditions: under N_2 atmosphere, the sample was annealed at 90 °C for 5 min and cooled to −20 °C at a rate of −10 K/min, then heated to 160 °C at a rate of 10 K/min.

Wide angle X-ray diffraction (WAXD): WAXD data were collected on an EMPYREAN diffractometer with Cu Kα radiation (λ = 1.54056 Å) over the 2θ range of 5–50° with a scan speed of 0.128548/s and a step size of 0.0083556° at room temperature.

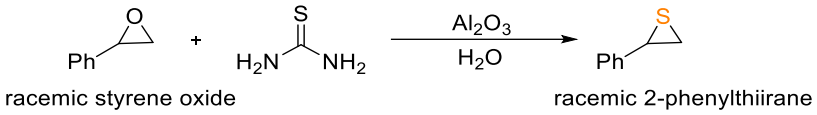
Dynamic mechanical analysis (DMA): A rectangular spline for the dynamic mechanical properties test with a scale of 20 mm × 4 mm × 0.1 mm was obtained by cutting the film. The test was performed at small tension film mode, 0.05% strain, 1 Hz, 3 °C/min on a Mettler-Toledo DMA/SDTA 1+.

Circular Dichroism (CD): CD spectra were recorded on a JASCO J-810

spectrometer. The light pathlength of the quartz cell used was 10 mm. The concentration was about 1×10^{-5} mol/L and the solvent was $CHCl_3$.

2. Synthesis of 2-phenylthiirane

2.1. Synthesis of racemic 2-phenylthiirane

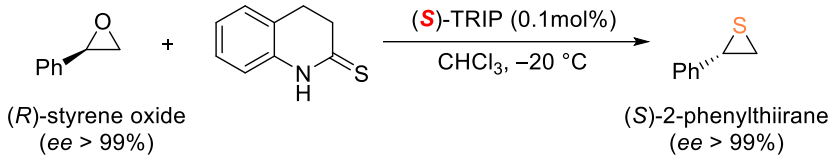


Scheme S1. Synthesis of racemic 2-phenylthiirane

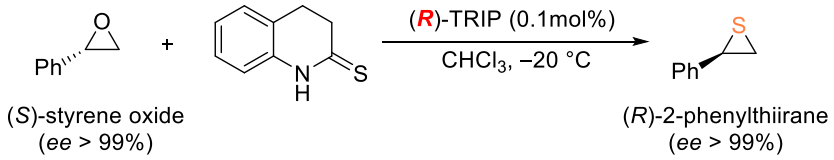
The synthesis of racemic 2-phenylthiirane (*rac*-PT) proceeds as following (Scheme S1): In a 500 mL round-bottom flask equipped with a magnetic stirrer, thiourea (76 g, 1.0 equiv.) was dispersed in 300 mL of water, followed by the addition of Al_2O_3 (3.0 g) as a catalyst. Subsequently, the corresponding racemic styrene oxide (*rac*-SO) (60 g, 0.5 equiv.) was added dropwise to the solution at 25 °C. After stirring for 8 hours, the solution was allowed to separate into layers to yield the corresponding *rac*-PT, which was then dried with CaH_2 twice before use.

***rac*-PT**: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.38 – 7.23 (m, 5H), 3.92 (dd, J = 6.5, 5.6 Hz, 1H), 2.90 (dd, J = 6.6, 1.5 Hz, 1H), 2.68 (dd, J = 5.6, 1.5 Hz, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 139.2, 128.7, 127.7, 126.9, 36.3, 27.4.

2.2. Synthesis of chiral 2-phenylthiirane



Scheme S2. Synthesis of (*S*)-2-phenylthiirane



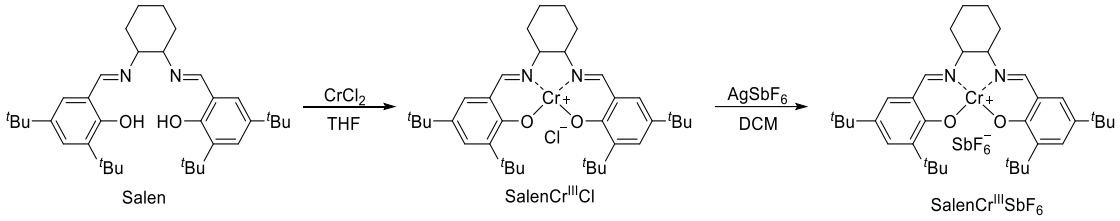
Scheme S3. Synthesis of (*R*)-2-phenylthiirane

The preparation methods of (*S*)-2-phenylthiirane ((*S*)-PT) (Scheme S2) and (*R*)-2-phenylthiirane ((*R*)-PT) (Scheme S3) are referenced in literature.[1] The reactions were conducted under standard conditions with 0.1 mol% catalyst, using enantioenriched

(*R*)-styrene oxide ((*R*)-SO) (*ee* > 99%). The reactions achieved over 99% conversion after 72 hours, and the (*S*)-PT was enantiomerically pure (*ee* > 99%).

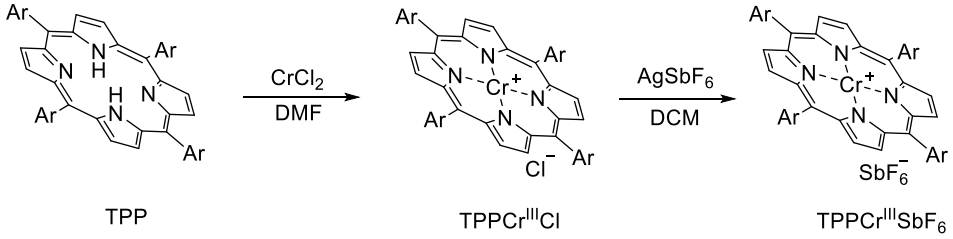
(*S*)-PT: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.38 – 7.23 (m, 5H), 3.92 (dd, J = 6.5, 5.6 Hz, 1H), 2.90 (dd, J = 6.6, 1.5 Hz, 1H), 2.68 (dd, J = 5.6, 1.5 Hz, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 139.2, 128.7, 127.7, 126.9, 36.3, 27.4.

3. Synthesis of SalenCr^{III}SbF$_6$ and TTPCr^{III}SbF$_6$



Scheme S4. Synthesis of SalenCr^{III}SbF$_6$

The SalenCr^{III}SbF$_6$ (Scheme S4) was prepared according to literature.[2]

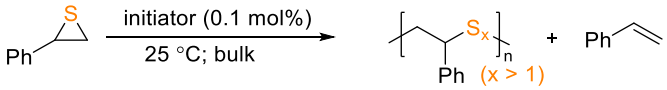


Scheme S5. Synthesis of TPPCr^{III}SbF$_6$

The TPPCr^{III}Cl (Scheme S5) was prepared according to literature,[3] and the method for converting TPPCr^{III}Cl to TTPCr^{III}SbF$_6$ is consistent with the aforementioned preparation of SalenCr^{III}SbF$_6$.

4. General procedure for the ROP of 2-phenylthiirane

4.1. The procedure for the AROP of 2-phenylthiirane



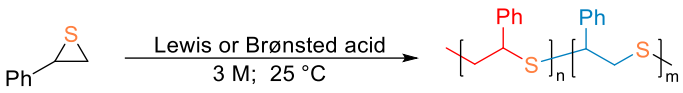
Scheme S6. The AROP of 2-phenylthiirane

The procedure for the anionic ring-opening polymerization (AROP) of PT is

described as following: In the glovebox with argon atmosphere, anionic initiator (0.015 mmol, 1 equiv.) and PT (15.0 mmol, 1000 equiv.) were added to a pre-dried 10 mL Schlenk tube equipped with a magnetic stirrer. The reaction tube was taken out from the glovebox after being sealed and put into the pre-heated oil bath, followed by stirring at 25 °C for an appropriate time. A small amount of the resultant mixture was removed from the Schlenk tube for ^{1}H NMR and GPC analysis to quantitatively determine the conversion of PT and molecular weight of PPT. The residual crude polymer was dissolved in DCM, precipitated with methanol. The solid was collected via filtering. This process was repeated for 3 times to ensure all the residual monomers removed. The obtained polysulfide was dried under vacuum at 50 °C prior to analysis *via* NMR, GPC, and Raman spectroscopy.

Polysulfide：^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.25 (m, 3H), 7.19 – 6.93 (m, 2H), 4.13 – 3.48 (m, 1H), 3.42 – 2.64 (m, 2H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 138.6, 128.9, 128.5, 128.4, 54.00, 53.6, 43.5, 43.2.

4.2. The procedure for the CROP of 2-phenylthiirane



Scheme S7. The CROP of 2-phenylthiirane.

The procedure for the cationic ring-opening polymerization (CROP) of PT is described as following: In the glovebox with argon atmosphere, PT (15.0 mmol, 1000 equiv.) and THF (PT = 3 M) were added to a pre-dried 10 mL Schlenk tube equipped with a magnetic stirrer. Subsequently, Lewis or Brønsted acid (0.015 mmol, 1 equiv.) was added. The reaction mixture was stirred at 25 °C for an appropriate time. A small amount of the resultant mixture was removed from the Schlenk tube for ^{1}H NMR and GPC analysis to quantitatively determine the conversion of PT and molecular weight of PPT. and the Schlenk tube was washed with DCM, and the combined phases were removed in vacuum. The residual crude polymer was dissolved in DCM, precipitated with methanol. The solid was collected via filtering. This process was repeated for 3 times to ensure all the residual monomers removed. The collected PPT was vacuum-dried at 50 °C prior to NMR, GPC, and DSC analysis.

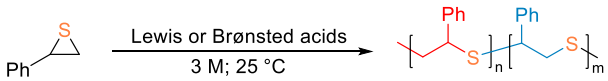
Atactic PPT：^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.21 (m, 3H), 7.10 – 6.94 (m,

2H), 3.56 – 3.27 (m, 1H), 2.69 – 2.40 (m, 2H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 140.9, 140.8, 140.5, 140.5, 128.6, 128.2, 128.0, 127.8, 50.9, 50.7, 50.5, 50.3, 50.2, 37.8, 37.7, 37.6, 37.5.

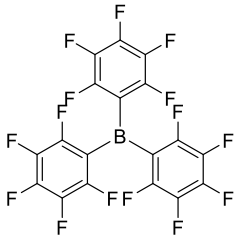
Isotactic PPT: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.23 (m, 3H), 7.08 – 6.96 (m, 2H), 3.32 (t, 1H), 2.60 – 2.43 (m, 2H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 140.8, 128.7, 128.3, 127.9, 50.7, 37.7.

5. Screening Lewis or Brønsted acids for the CROP of PT

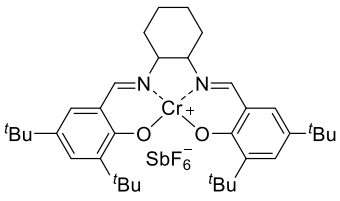
Table S1. Screening Lewis or Brønsted acids for the CROP of PT.[a]



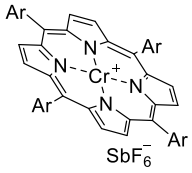
Lewis or Brønsted acids:



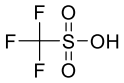
($B(C_6F_5)_3$)



($SalenCr^{III}SbF_6$)



($TPPCr^{III}SbF_6$)



(TfOH)

entry	acids	time [h]	conversion[b] [%]	HT[c] [%]	M_n[d] [kg/mol]	$Đ$[d] [M_w/M_n]
1	$BF_3{\cdot}Et_2O$	0.3	>99	98	120.2	1.85
2	$B(C_6F_5)_3$	3	75	92	49.1	1.79
3	$SalenCr^{III}SbF_6$	0.1	>99	95	60.5	1.75
4	$TPPCr^{III}SbF_6$	3	89	97	86.2	1.99
5	TfOH	0.1	>99	88	28.8	1.71
6	$ZnCl_2$	24	<1	–[e]	–[e]	–[e]
7	$AlCl_3$	24	<1	–[e]	–[e]	–[e]
8	BBr_3/MOMBr	24	<1	–[e]	–[e]	–[e]

[a]Conditions: The reaction was performed in neat PT (2.0 g, 15.0 mmol) in a 10 mL vial at 25 °C, with a feed ratio of PT/acid = 1000/1 (molar ratio). [b]Determined by ^{1}H NMR spectroscopy based on PT. [c]Determined by ^{13}C NMR spectroscopy, the HT linkage contents in the PPTs are calculated using formula S1. [d]Determined by gel permeation chromatography in THF, calibrated with polystyrene. [e]Not detected.

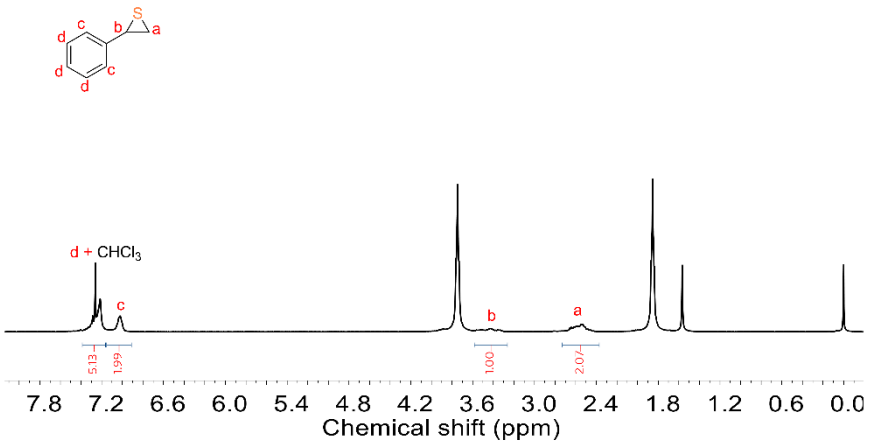


Fig. S1. ^{1}H NMR spectrum of reaction mixture of the $BF_3{\cdot}Et_2O$-catalyzed CROP of PT.

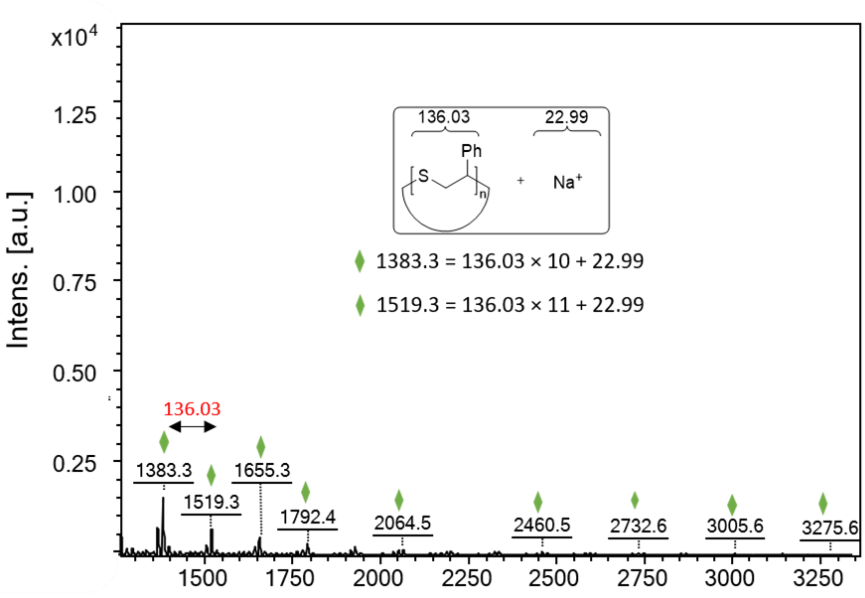


Fig. S2. MALDI-TOF-MS analysis of PPT.

The sequence structure of resultant PPT was further characterized using matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF-MS). Taking the PPT with a M_n of 2.5 kg/mol synthesized using $BF_3{\cdot}Et_2O$ as catalyst as example, a series of peaks with an interval of *m/z* 136.03, equivalent to the molecular weight of PT, are observed from the MALDI-TOF-MS spectrum (Fig. S2).

6. The determination of HT linkages using ^{13}C NMR spectroscopy

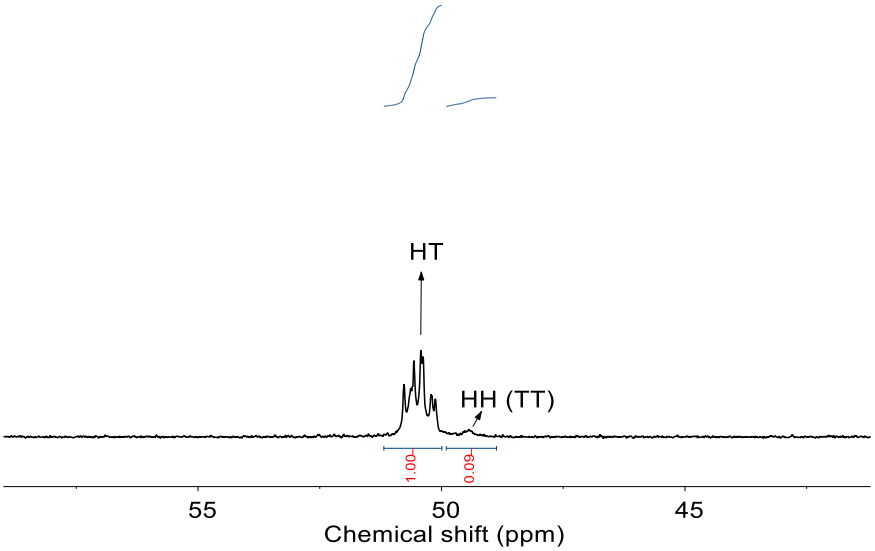


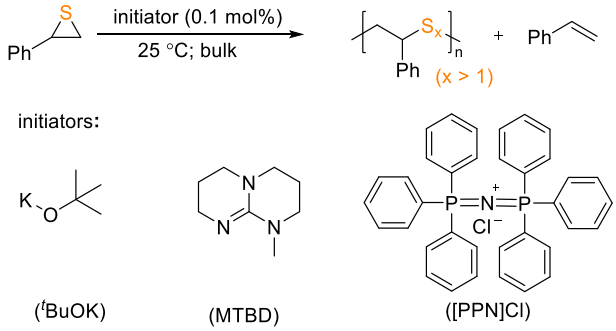
Fig. S3. ^{13}C NMR spectrum of methine region of PPT.

$$HT = \frac{Area_{HT}}{Area_{HT} + Area_{HH}} \times 100\% \qquad \text{formula S1}$$

The ^{13}C NMR spectrum of PPT displays fine structural features originating from regiochemical in the polymer chain (Fig. S3). The methine region of PPT in the ^{13}C NMR spectrum shows two distinct chemical shifts, which can be utilized to determine the Head-to-Tail (HT) linkage content according to formula S1. Taking the PPT synthesized using $B(C_6F_5)_3$ as catalyst (Table S1, entry 2), the HT content is calculated as 1 / (1 + 0.09) × 100% = 92%.

7. Screening initiators for the AROP of PT

Table S2. Screening initiators for the AROP of PT.[a]



entry	initiator	time [h]	conversion[b] [%]	M_n[c] [kg/mol]	$Đ$[c] [M_w/M_n]
1	^{t}BuOK	16	80	20.2	1.79
2	MTBD	0.15	>99	97.0	1.89
3	[PPN]Cl	12	<1	–[d]	–[d]

[a]Conditions: The reaction was performed in neat PT (2.0 g, 15.0 mmol) in a 10 mL vial at 25 °C, with a feed ratio of PT/initiator = 1000/1 (molar ratio). [b]Determined by ^{1}H NMR spectra based on PT. [c]Determined by gel permeation chromatography in THF, calibrated with polystyrene. [d]Not detected.

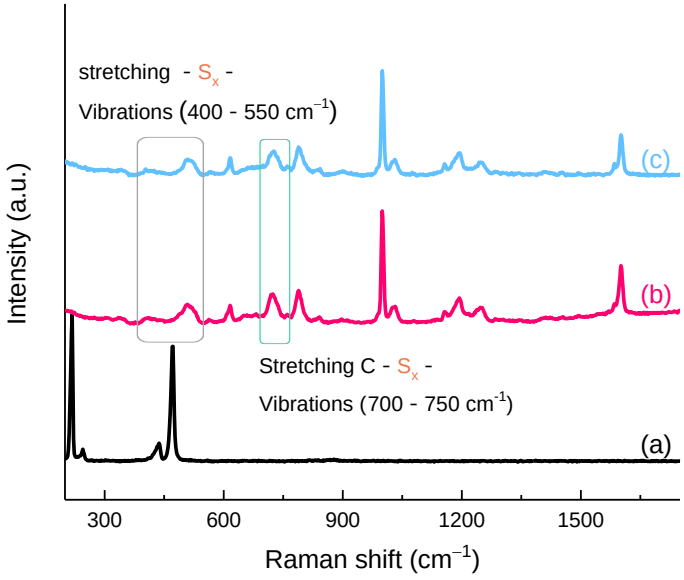


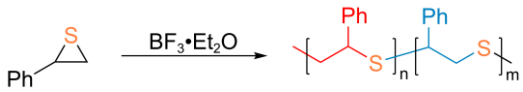
Fig. S4. Raman spectra of (a) elemental sulfur, (b) polysulfides synthesized from the ^{t}BuOK-initiated AROP of PT, and (c) polysulfides synthesized from the MTBD-initiated AROP of PT.

In the AROP, ^{t}BuOK, MTBD, and [PPN]Cl were used as anionic initiators (Table S2). The Raman spectra for the polysulfides initiated by ^{t}BuOK and MTBD displayed the stretching vibration peaks of –S_x– at 400 – 500 cm^{-1}, and

stretching vibration peaks of –C–S_x– at 700 – 750 cm^{-1} (Fig. S4). However, [PPN]Cl was ineffective in initiating the polymerization of PT.

8. Optimization conditions for the CROP of PT catalyzed by $BF_3{\cdot}Et_2O$

Table S3. Optimization conditions for the CROP of PT catalyzed by $BF_3{\cdot}Et_2O$.[a]

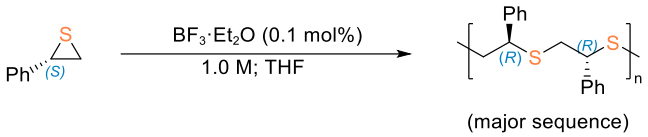


entry	temperature [°C]	concentration [M]	time [h]	conversion[b] [%]	HT[c] [%]	M_n[d] [kg/mol]	$Đ$[d] [M_w/M_n]
1	25	3	0.3	>99	98	120.2	1.85
2	25	2	0.3	78	98	143.0	1.91
3	25	1.5	0.3	63	98	121.2	1.84
4	25	1	2	57	98	86.1	1.44
5	0	3	3	>99	99	137.6	2.06
6	−20	3	6.5	>99	>99	131.6	2.12

[a]Conditions: The reaction was carried out in neat PT (2.0 g, 15.0 mmol) and THF in a 10 mL vial at 25 °C. The $BF_3{\cdot}Et_2O$ to PT ratio was 1/1000 (molar ratio). [b]Determined by ^1H NMR spectroscopy based on PT. [c]Determined by ^{13}C NMR spectroscopy, the HT linkage contents in the PPTs are calculated using formula S1. [d]Determined by gel permeation chromatography in THF, calibrated with polystyrene.

9. Outputs of the CROP of chiral PT catalyzed by $BF_3{\cdot}Et_2O$

Table S4. Outputs of the CROP of chiral PT catalyzed by $BF_3{\cdot}Et_2O$.[a]

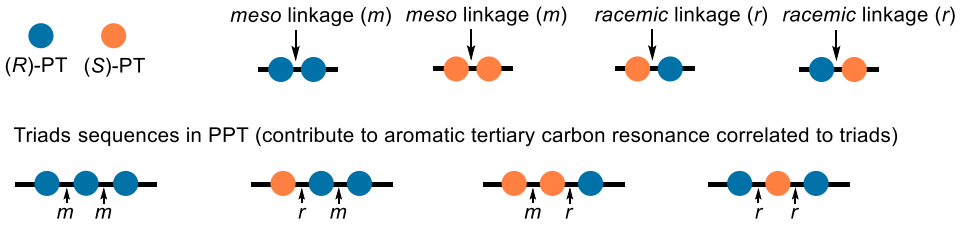


(major sequence)

entry	configuration	$[\alpha]_D^{20}$ [b] [°]	temp. [°C]	time [h]	conv.[c] [%]	HT[d] [%]	[*mm*][d] [%]	P_m[d] [%]	$[\alpha]_D^{20}$ [b] [°]	M_n[e] [kg/mol]	$Đ$[e] [M_w/M_n]
1	*rac*-	0	-20	24	>99	>99	–[f]	–[f]	0	75.9	1.63
2	(*S*)-	+435	25	2	>99	>99	78	88	−633	66.2	1.67
3	(*S*)-	+435	0	11	>99	>99	88	94	−765	63.7	1.72
4	(*S*)-	+435	-20	24	97	>99	>99	>99	−990	72.5	1.95
5	(*R*)-	−442	-20	24	93	>99	>99	>99	+982	70.3	2.06

[a]Conditions: The reaction was performed in neat (*R*)- or (*S*)-PT (*ee* > 99%) (1.0 g, 7.5 mmol) and THF in a 10 mL vial. The $BF_3{\cdot}Et_2O$ to PT ratio was 1/1000 (molar ratio). [b]Conditions: the test performed at the concentration is 1 g/100 mL and the temperature is 20 °C. [c]Determined by ^{1}H NMR spectra based on PT. [d][*mm*] is isotactic triad made up of two adjacent *meso* diads, determined by ^{13}C NMR spectroscopy, based on the PPTs (formula S2). [d]P_m is the probability of *meso* linkages between PPT units, determined by ^{13}C NMR spectroscopy (formula S3). [e]Determined by using gel permeation chromatography in THF, calibrated with polystyrene. [f]Not detected.

10. The determination of P_m and [*mm*] using ^{13}C NMR spectroscopy



mm is isotactic sequence made up of two adjacent *meso* (***m***) diads
rm is heterotactic sequence made up of adjacent *racemic* (***r***) diad and *meso* (***m***) diad
mr is heterotactic sequence made up of adjacent *meso* (***m***) diad and *racemic* (***r***) diad
rr is syndiotactic sequence made up of two adjacent *racemic* (***r***) diads

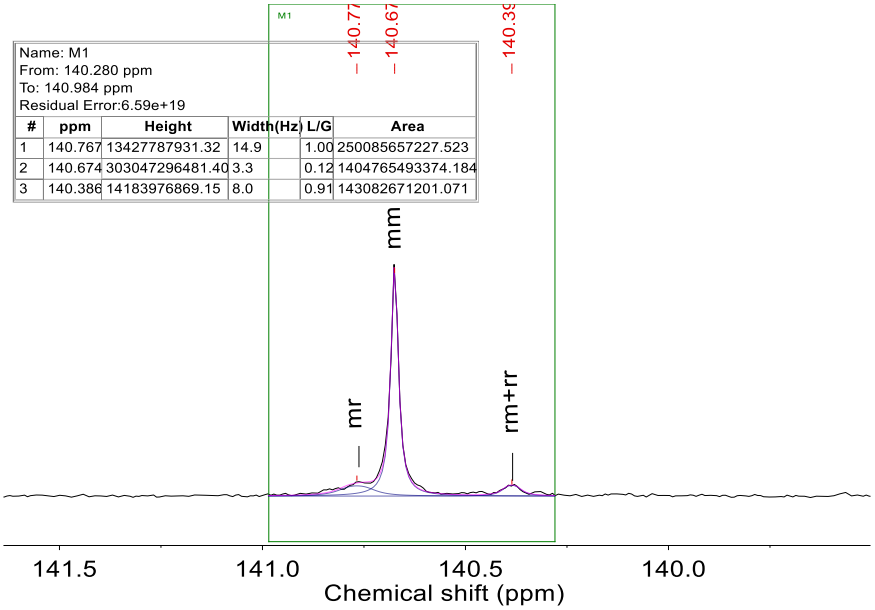


Fig. S5. ^{13}C NMR spectra of the aromatic tertiary carbon region of PPT.

$$[mm] = \frac{Area_{mm}}{(Area_{mr} + Area_{mm} + Area_{rm} + Area_{rr})} \times 100\% \qquad \text{formula S2}$$

$$P_{\mathrm{m}} = \sqrt{\frac{Area_{mm}}{Area_{mr} + Area_{mm} + Area_{rm} + \mathrm{Area_{rr}}}} \times 100\% \qquad \text{formula S3}$$

The peaks in ^{13}C NMR spectra of PPT synthesized in this manuscript exhibit fine structure that results from stereo-microstructures in the PPTs. The ^{13}C NMR spectra of the aromatic tertiary carbon region of PPT exhibit triads, which can be used to calculate [*mm*] and P_{m}. [*mm*] was calculated using formula S2, and P_{m} was calculated using formula S3. Here, [*mm*] is isotactic triad made up of two adjacent *meso* diads. P_{m} is the probability of *meso* linkages between PPT units. Taking the PPT (Table S4, entry 2) for example, the [*mm*] = 140.47 / (140.47 + 25.01 + 14.31) × 100% = 78%; P_{m} = [140.47 / (140.47 + 25.01 + 14.31)]$^{1/2}$ × 100% = 88%.

11. ^{13}C NMR and ^{1}H NMR spectra of PPTs with different isotacticities

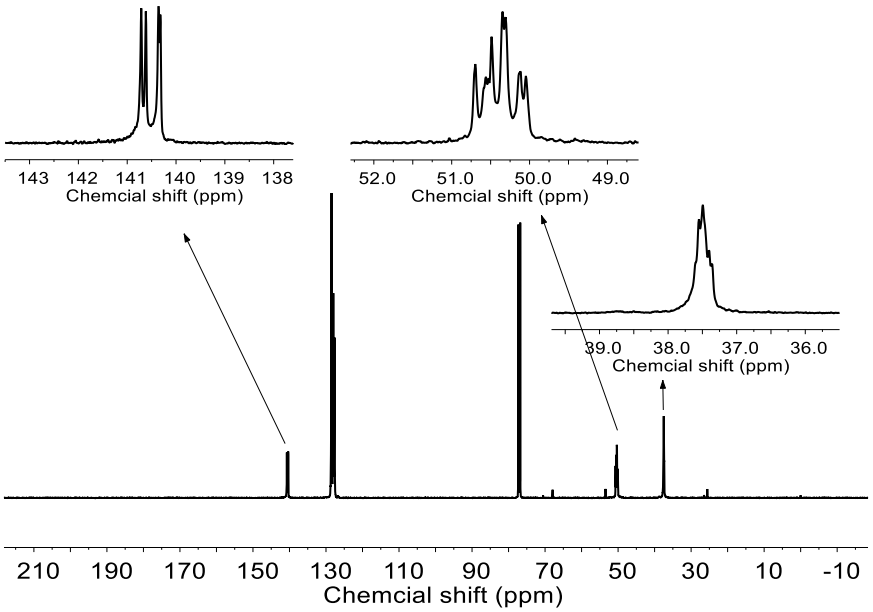


Fig. S6. ^{13}C NMR spectrum of atactic PPT synthesized from *rac*-PT at 25 °C.

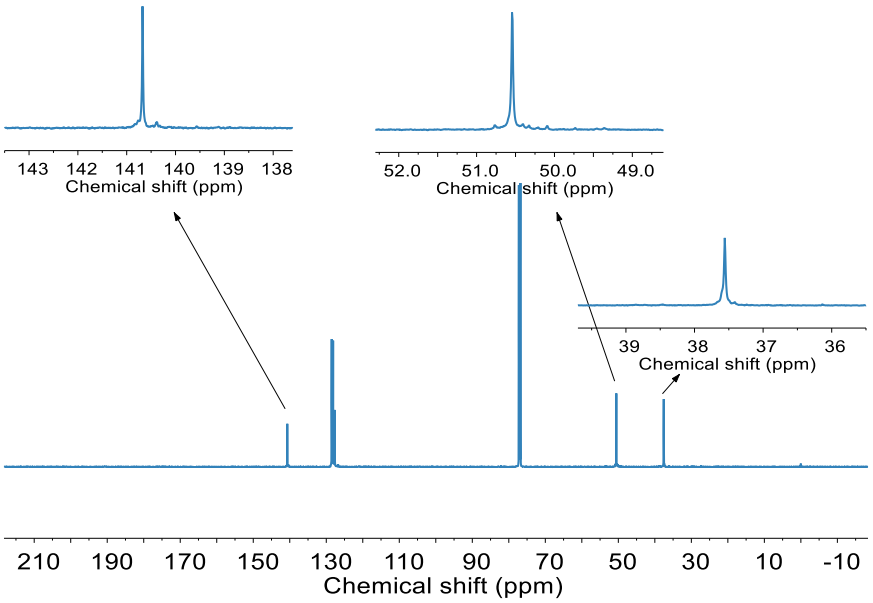


Fig. S7. ^{13}C NMR spectrum of PPT with P_m of 88% synthesized from (*S*)-PT at 25 °C.

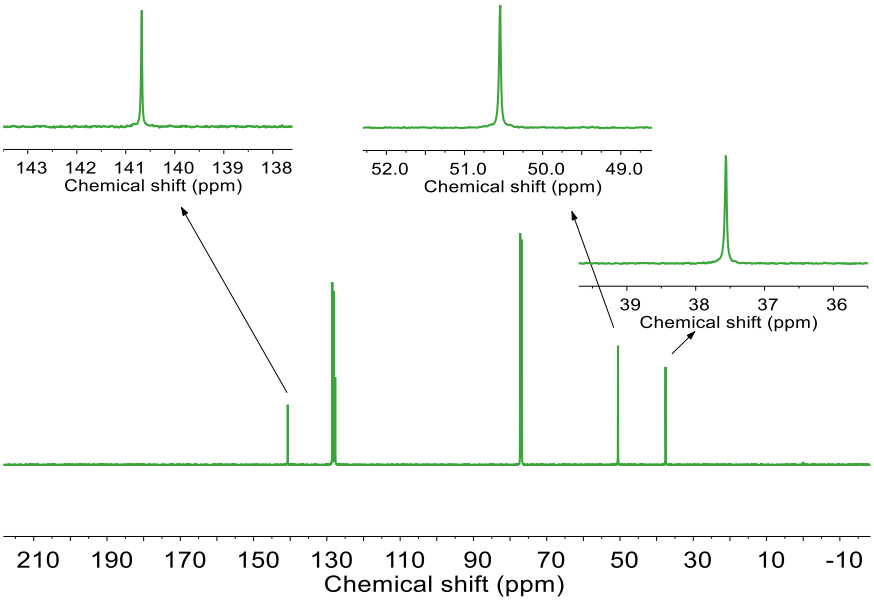


Fig. S8. ^{13}C NMR spectrum of PPT with P_m of > 99% synthesized from (*S*)-PT at −20 °C.

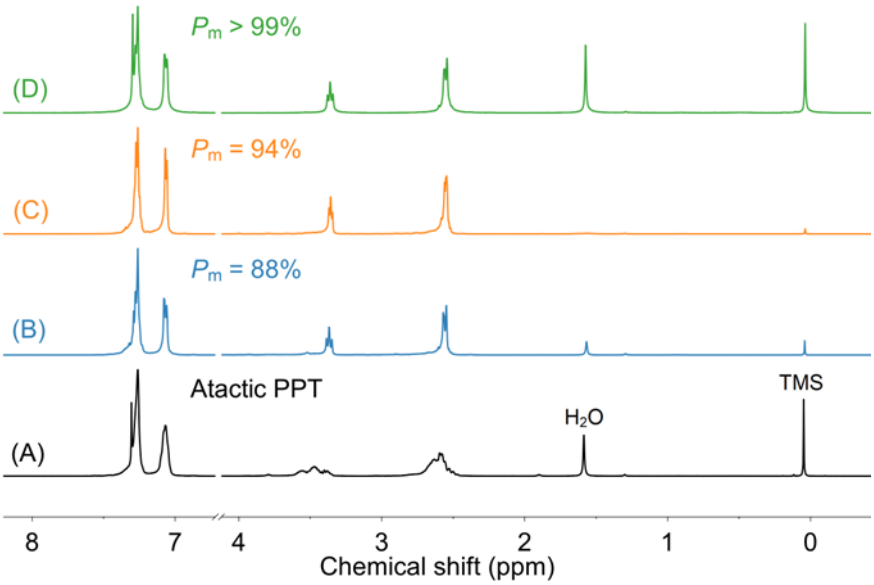


Fig. S9. ^{1}H NMR spectra of different isotacticities: (A) atactic PPT synthesized from *rac*-PT at 25 °C, (B) PPT with P_m of 88% synthesized from (*S*)-PT at 25 °C, (C) PPT with P_m of 94% synthesized from (*S*)-PT at 0 °C, (D) PPT with P_m of > 99% produced by (*S*)-PT and performed at −20 °C.

12. The CD spectra of chiral 2-phenylthiirane and isotactic PPT

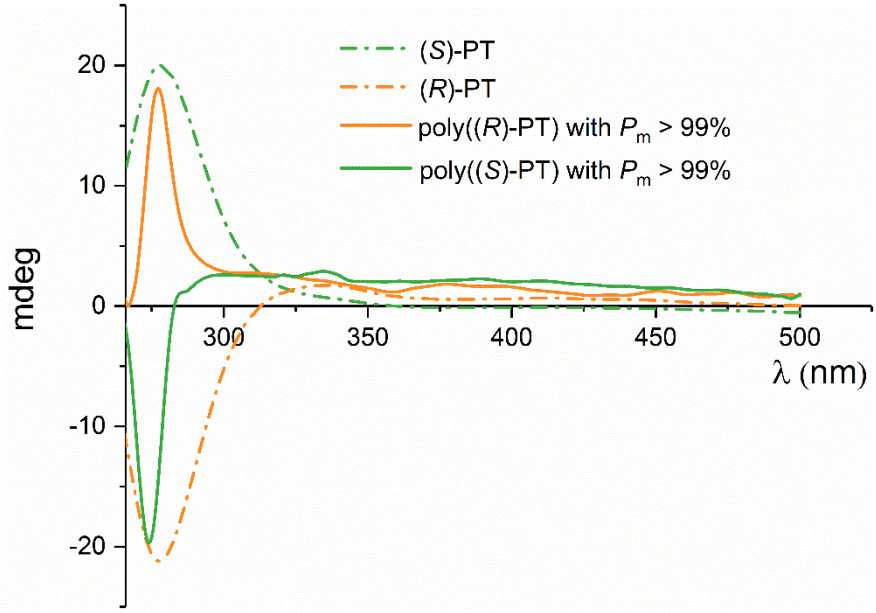


Fig. S10. CD spectra of (*R*)- and (*S*)-PT and resulting PPT with P_m of > 99%.

13. ^{1}H and ^{13}C NMR spectra of 2-phenylthiirane, PPT and polysulfide

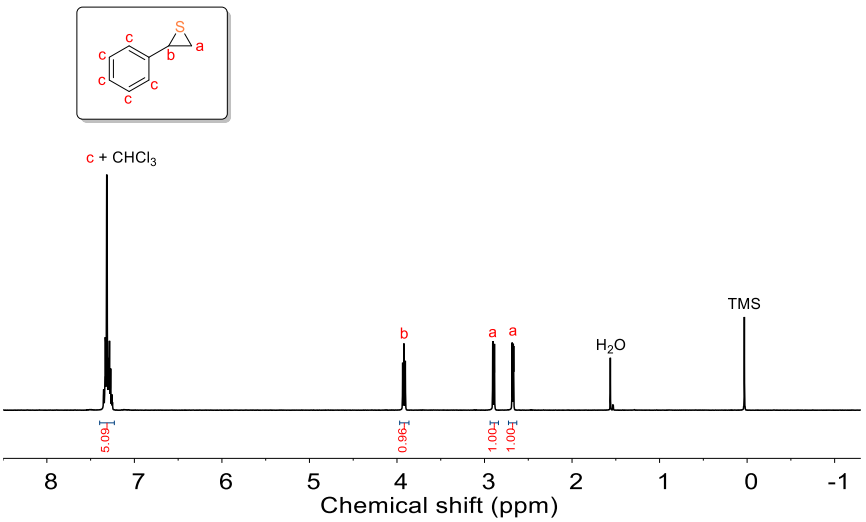


Fig. S11. ^{1}H NMR spectrum of PT in $CDCl_3$.

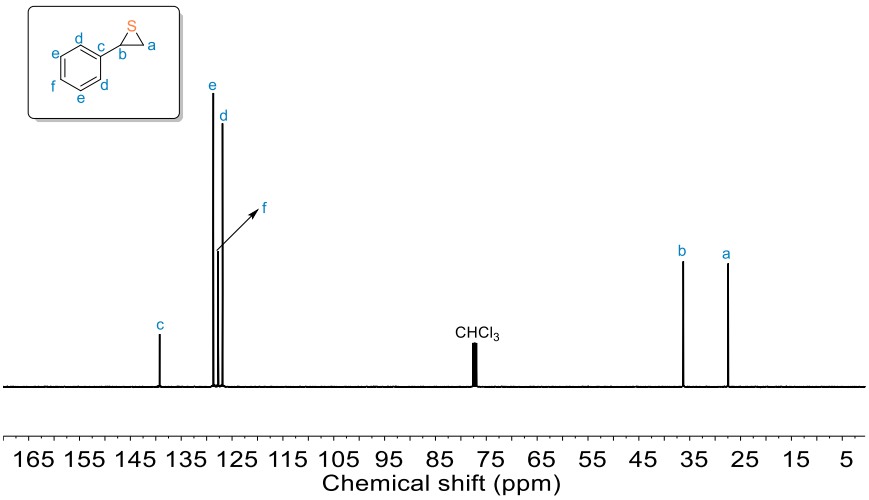


Fig. S12. ^{13}C NMR spectrum of PT in $CDCl_3$.

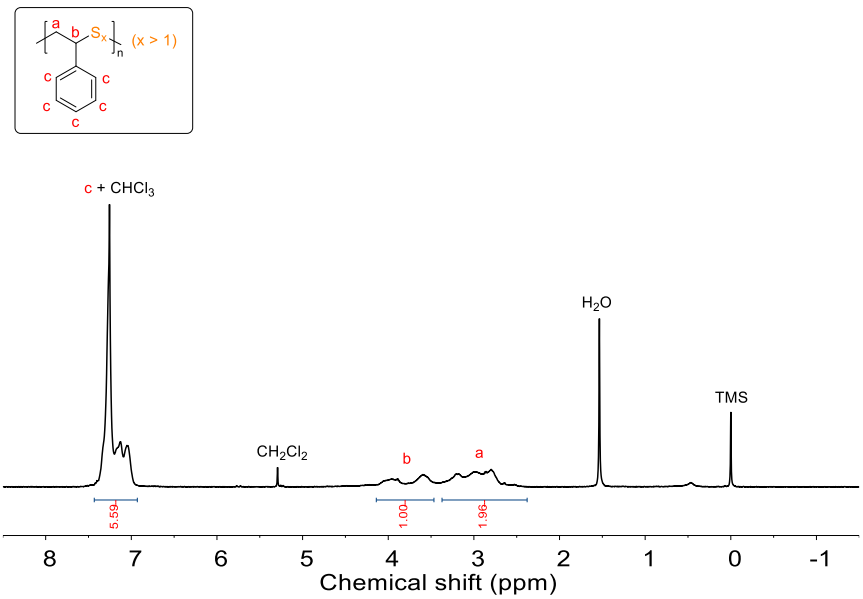


Fig. S13. ^{1}H NMR spectrum of polysulfide in $CDCl_3$.

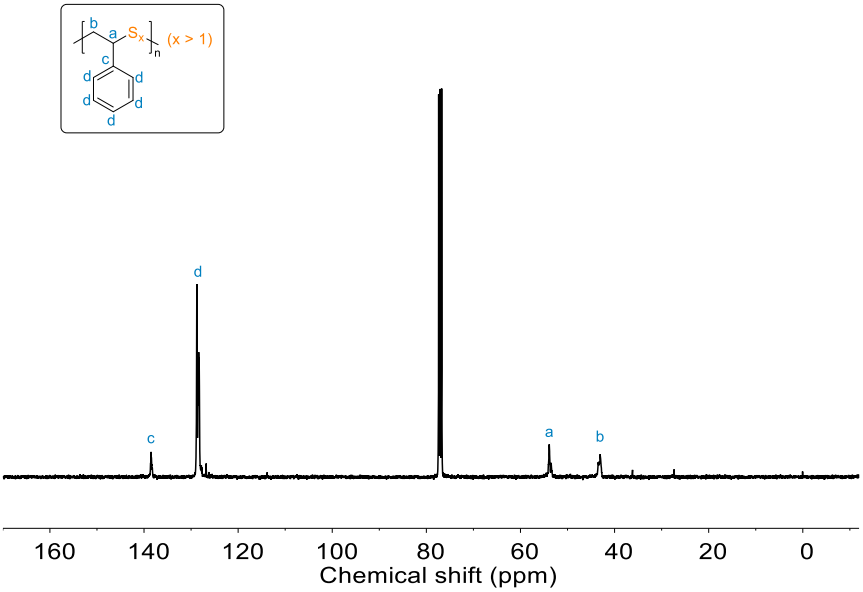


Fig. S14. ^{13}C NMR spectrum of polysulfide in $CDCl_3$.

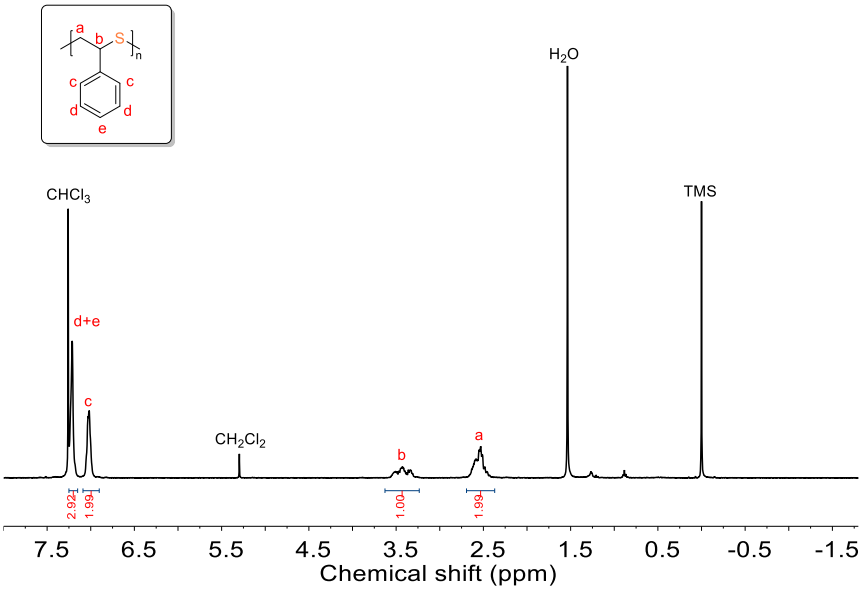


Fig. S15. ^{1}H NMR spectrum of atactic PPT in $CDCl_3$.

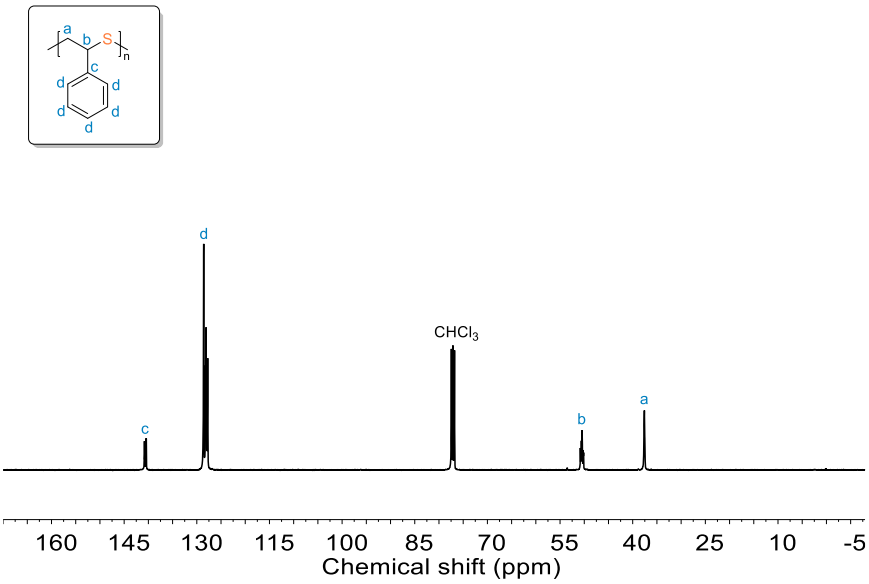


Fig. S16. ^{13}C NMR spectrum of PPT in $CDCl_3$.

14. References

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