Organocatalytic Selective Coupling of Episulfides with Carbon Disulfide for the Synthesis of Poly(trithiocarbonate)s and Cyclic Trithiocarbonates

Chao Chen, Yves Gnanou, and Xiaoshuang Feng**

Physical Sciences and Engineering Division, King Abdullah University of Science and Technology (KAUST), Thuwal 23955, Saudi Arabia

* E-mail: yves.gnanou@kaust.edu.sa; fxs101@gmail.com

Contents

Experimental section 3

Figure S1. ^{1}H NMR spectrum of propylene sulfide in $CDCl_3$...6

Figure S2. ^{13}C NMR spectrum of propylene sulfide in $CDCl_3$..7

Figure S3. ^{1}H NMR spectrum of crude polymer solution, entry 2 Table 1. 8

Figure S4. FTIR spectra of the linear polytrithiocarbonate (top) and cyclic trithiocarbonate (bottom). 9

Figure S5. ^{1}H NMR spectrum of precipitated PPSC that was obtained in the presence of DoSH, entry 12 Table 1. 10

Figure S6. *In-situ* FTIR surface image in the range of 950-1150 cm^{-1} for the copolymerization of PS and CS_2. 11

Figure S7. ^{1}H NMR spectrum of CHS in $CDCl_3$. 11

Figure S8. ^{1}H NMR spectrum of CHS based cyclic trithiocarbonate in $CDCl_3$. 12

Figure S9. ^{1}H NMR spectrum of ES based cyclic trithiocarbonate in $CDCl_3$. 12

Figure S10. ^{1}H NMR spectrum of AES in $CDCl_3$. 13

Figure S11. ^{1}H NMR spectrum of AES based cyclic trithiocarbonate in $CDCl_3$. 13

Figure S12. ^{1}H NMR spectrum of PES in $CDCl_3$. 14

Figure S13. ^{1}H NMR spectrum of PES based cyclic trithiocarbonate in $CDCl_3$. 14

Figure S14. ^{1}H NMR spectrum of iBS in $CDCl_3$. 15

Figure S15. ^{1}H NMR spectrum of iBS based cyclic trithiocarbonate in $CDCl_3$. 15

Figure S16. DSC curve for the PPSC under N_2. 16

Figure S17. TGA curve for the PPSC under N_2. 16

Figure S18. DSC curve for the PESC under N_2..........17

Figure S19. TGA curve for the PESC under N_2. 17

Figure S20. ^{1}H NMR spectra of the linear poly(trithiocarbonate) treated with UV at different times. 18

Figure S21. ^{1}H NMR spectrum of the low molar mass poly(trithiocarbonate)s synthesized using 1,10-decanedithiol as chain transfer agent..........19

Figure S22. ^{1}H NMR spectrum of degradable polyethylene synthesized by polycondensation of poly(trithiocarbonate)s with hexamethylene diisocyanate. 20

Figure S23. FTIR spectra of the poly(trithiocarbonate) (red) and poly(thiourethane) (black)...........21

Figure S24. TGA curve for the poly(thiourethane) under N_2. 21

Figure S25. SEC traces of low molar mass poly(trithiocarbonate), poly(thiourethane) and degraded poly(thiourethane)..........22

Experimental section

Materials

All the reagents were purchased from Sigma-Aldrich and used as received unless otherwise stated. 1-*tert*-Butyl-4,4,4-tris(dimethylamino)-2,2-bis[tris(dimethylamino)-phosphoranylidenamino]-2λ^5,4λ^5-catenadi(phosphazene) (P_4, 0.8 M in hexane). Bis(triphenylphosphine)iminium chloride (PPNCl) was purified through recrystallization from diethyl ether three times and followed by drying under vacuum to remove the solvents. Tetrabutylammonium bromide (TBABr), tetrabutylammonium iodide (TBAI) and tetrabutylammonium acetate (TBAAc) were recrystallized from cold n-hexane and dried under vacuum. The traces of water in the above ammonium salts were removed by drying under vacuum in the presence of P_2O_5 for 2 days. Episulfides were synthesized as literature reported (Schurig, V.; Buerkle, W. *J. Am. Chem. Soc.* **1982**, *104*, 7573-7580). Carbon disulfide (CS_2), propylene sulfide, ethylene sulfide and solvent were purified by distilling over CaH_2. The purified monomers and ammonium salts were stored in Schlenk flasks and kept in glovebox. Benzyl alcohol (BnOH), tert-Butyl alcohol (tBuOH) and 1-Dodecanethiol (DoSH) were used before three times of freeze-pump-thaw degassing process.

Instruments

Nuclear magnetic resonance (NMR): ^{1}H and ^{13}CNMR spectra were recorded on a Bruker AVANCE III-400 Hz instrument in $CDCl_3$.

Gel permeation chromatography (GPC): GPC traces were acquired on a VISCOTEK VE2001 system equipped with the Styragel HR2 THF and Styragel HR4 THF using THF (1 mL/min) as the eluent. The relative molar masses and distributions were obtained at 35 °C using a RID detector and against linear polystyrene standards with molar mass ranging from 474 g/mol to 2.5×10^6 g/mol (concentration of samples injected is 5 mg/mL).

Fourier-transform infrared spectroscopy (FTIR): FTIR spectra were recorded on a NICOLET iS10 (Thermo Fisher Scientific) spectrometer. In situ FTIR study of the copolymerization of episulfide with CS2 was conducted via a ReactIR 700 system (Mettler Toledo).

Differential scanning calorimetry (DSC): DSC measurements were performed at a heating rate of 10 °C/min on a Mettler Toledo DSC1/TC100 system under nitrogen atmosphere. The curve of the second heating scan was adopted to determine the glass transition temperature (T_g).

Thermogravimetric analysis (TGA): TGA experiments were performed on a TGA Q500 analyzer (TA Instruments). Samples were heated from 25 °C to 800 °C at a heating rate of 10 °C/min under N_2 atmosphere.

Refractive index was determined via an A. Kruss Abbe-refractometer at 25 °C.

UV degraded reaction was performed using a Kessil PR160 LED (λ=370 nm, maximum power 40 W)

Synthesis of episulfides.

Take propylene sulfide as an example: in a 500 mL round-bottomed flask equipped with a magnetic stirbar, potassium thiocyanate (167 g , 1.72 mol, 2.0 eq.) was dispersed into 300 mL water. After the above salt fully dissolved, propylene oxide (50 g, 1.0 eq.) was added dropwise to the solution stirred for 2 h at 0 °C. And then, the solution was stirred overnight at room temperature. Propylene sulfide was collected by separating the hydrophobic phase from aqueous phase without further purification (Figure S1, Figure S2).

Copolymerization of CS_2 with propylene sulfide.

The typical copolymerization procedure for Entry 1 is described below. A 50 mL Schlenk tube was flame-dried and then immediately transferred into glovebox. The initiator (benzyl alcohol, 1 eq. molar), 1 eq. molar of P_4 (0.8 M in hexane), 600 eq. molar CS2 and 100 eq. molar of PS were added to the Schlenk tube respectively. Afterwards, the reaction was carried out at 0 °C for 12 h. The polymerization was quenched with few drops of 1 M HCl solution (methanol). An aliquot of crude solution was taken for SEC and ^{1}H NMR analysis. Pure polymer was obtained by three times' precipitation in methanol followed by overnight drying under vacuum.

Polymer degradability triggered by a radical source.

Pure poly(trithiocarbonate) and AIBN (5 % wt.) were dissolved in THF. The polymer solution was added into a Schlenk tube and degassed via three times of freeze-pump-thaw. And then the tube was immersed in oil bath at 70 °C. Samples were taken from the solution at different time interval for ^{1}H NMR characterization.

Polycondensation of oligo trithiocarbonate with HDI and its degradation by radical.

A 50 mL Schlenk tube was flame-dried and then immediately transferred into glovebox. Oligo trithiocarbonate (500 mg, 1.0 eq.), HDI (105 mg, 1.0 eq.) and dibutyltin dilaurate (4 mg, 0.01 eq.) were added to the Schlenk tube. The reaction was carried out at 60 °C overnight. Polymer was purified by precipitating in methanol and dried under vacuum (yield 91 %). SEC showed a unimodal with molar mass 35 kg/mol and *Đ* 1.35.

The above obtained polythiourethane (100 mg) and AIBN (5 mg, 5 % wt.) were dissolved in DMF and added in a Schlenk tube. After three times of freeze-pump-thaw degassing procedure the tube was immersed in oil bath at 70 °C overnight. Samples were taken from the solution for SEC characterization.

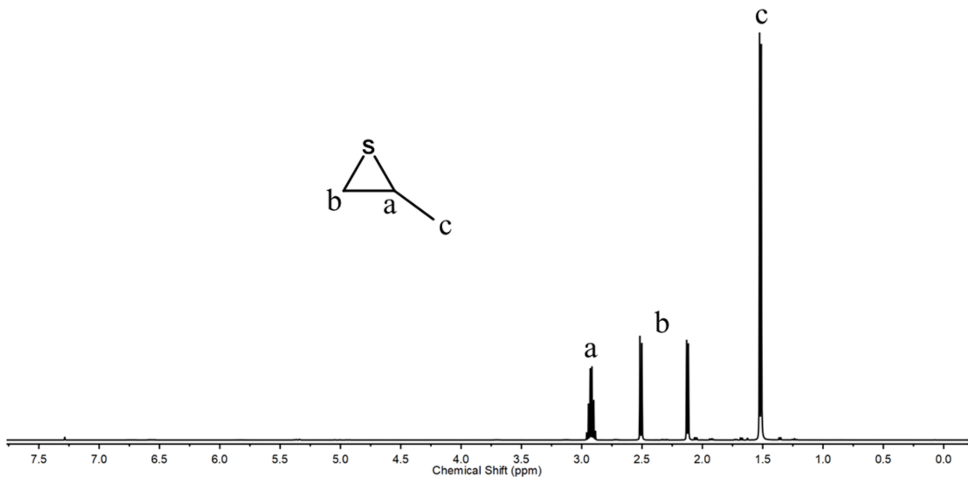


Figure S1. ^{1}H NMR spectrum of propylene sulfide in $CDCl_3$.

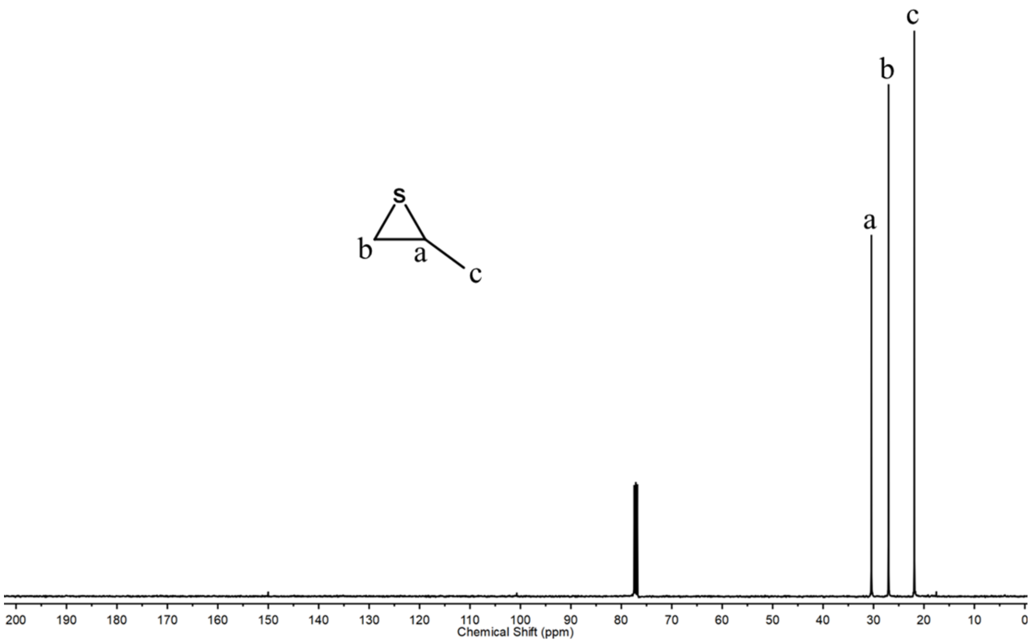


Figure S2. ^{13}C NMR spectrum of propylene sulfide in $CDCl_3$.

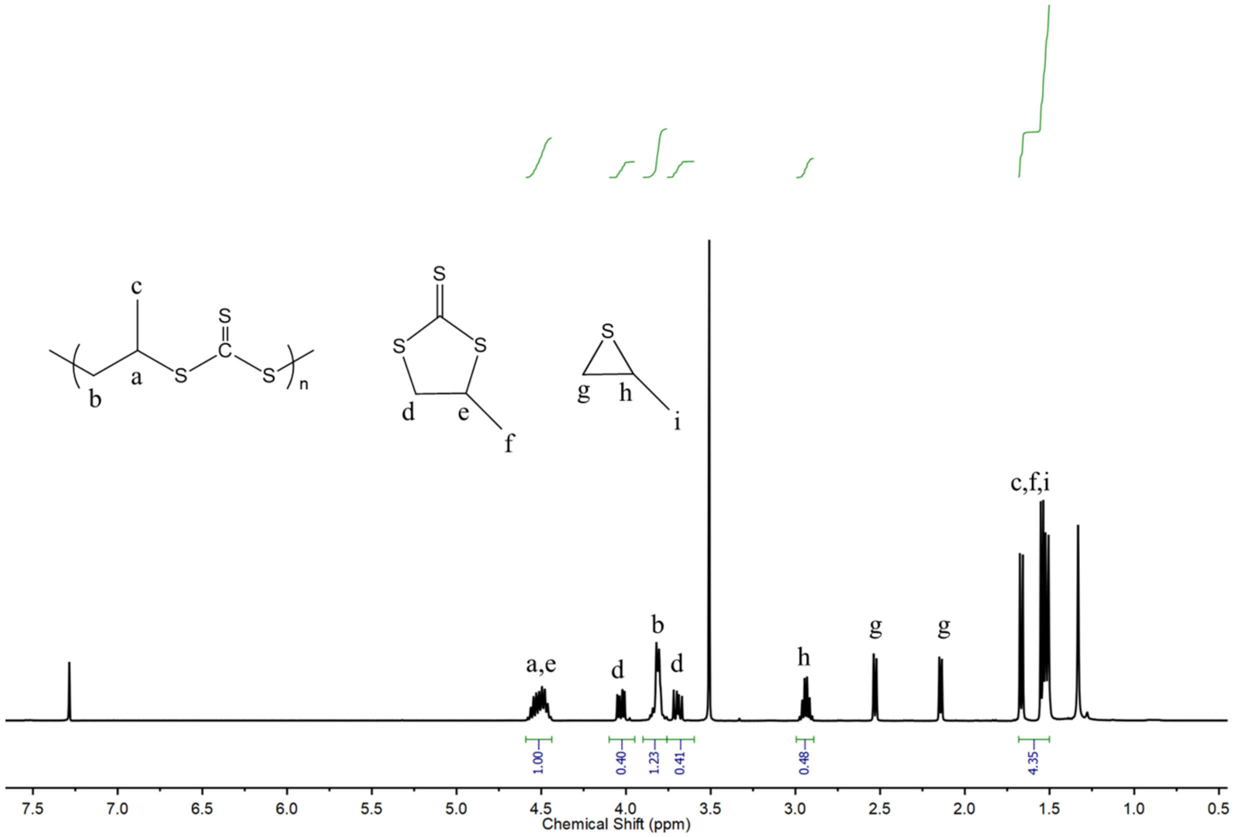
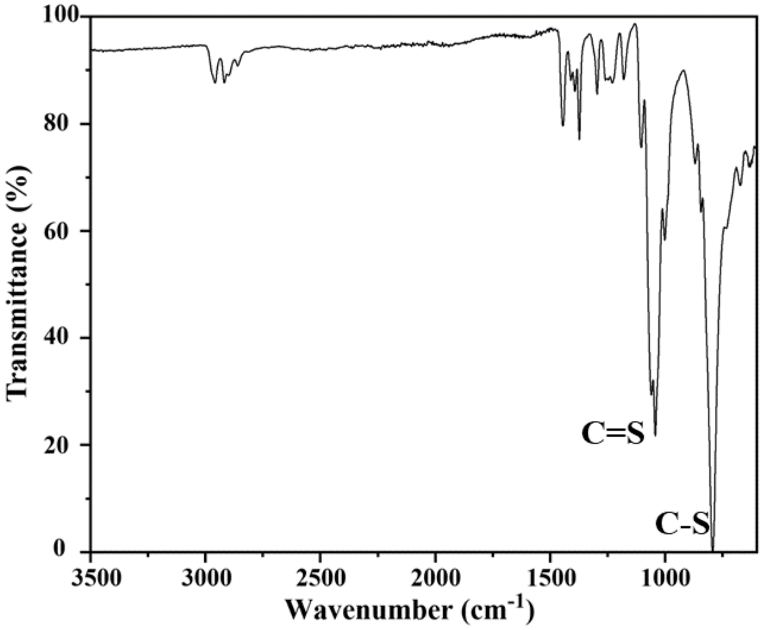


Figure S3. ^{1}H NMR spectrum of crude polymer solution, entry 2 Table 1.



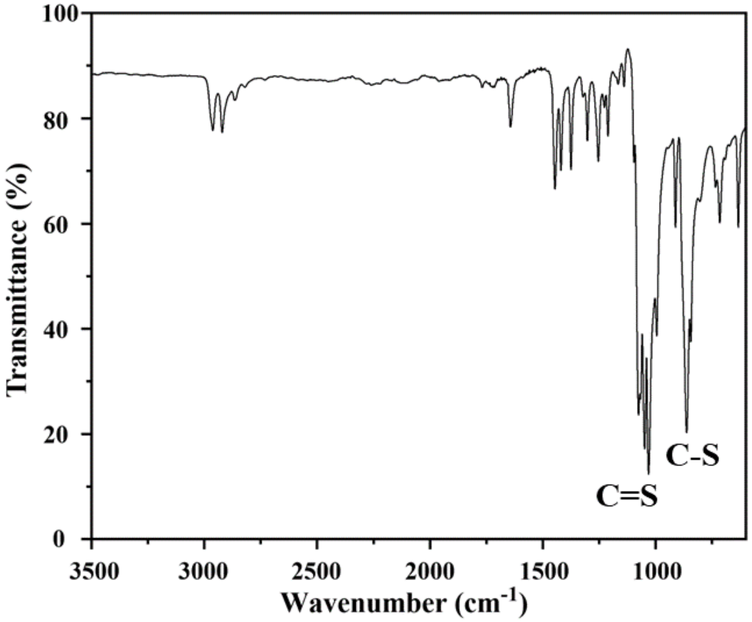


Figure S4. FTIR spectra of the linear polytrithiocarbonate (top) and cyclic trithiocarbonate (bottom).

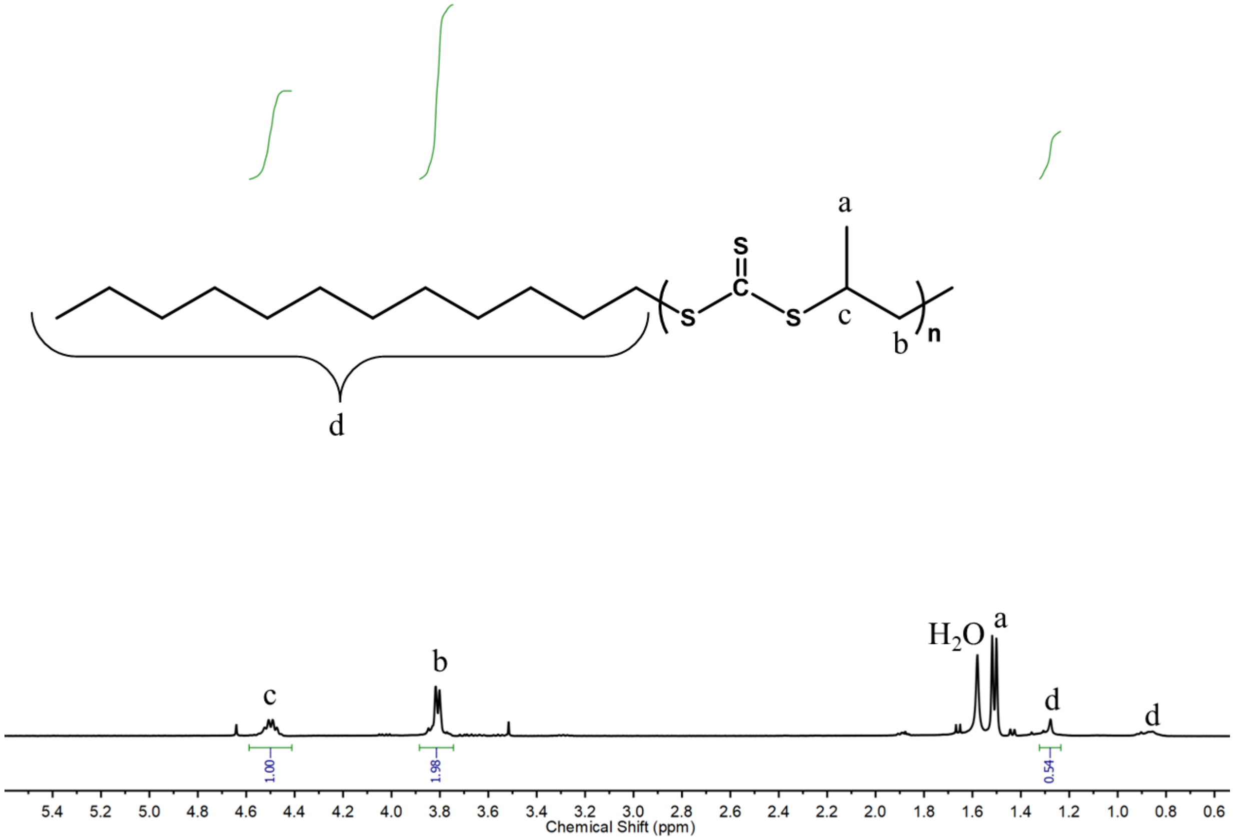


Figure S5. ^{1}H NMR spectrum of precipitated PPSC that was obtained in the presence of DoSH, entry 12 **Table 1**.

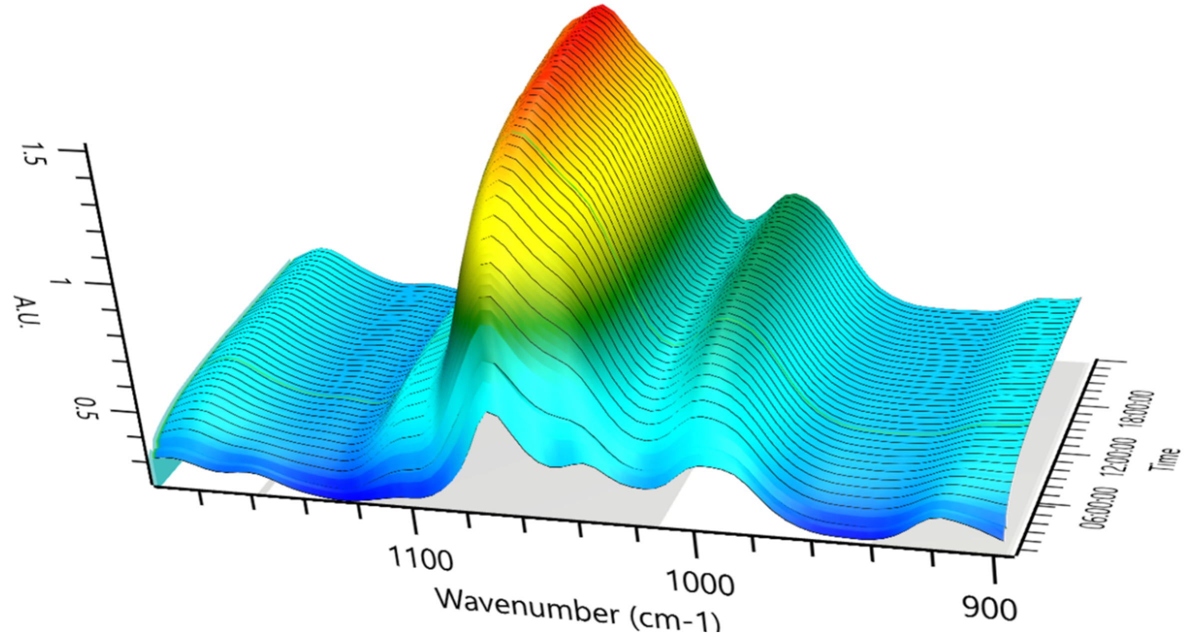


Figure S6. *In-situ* FTIR surface image in the range of 950-1150 cm^{-1} for the copolymerization of PS and CS_2.

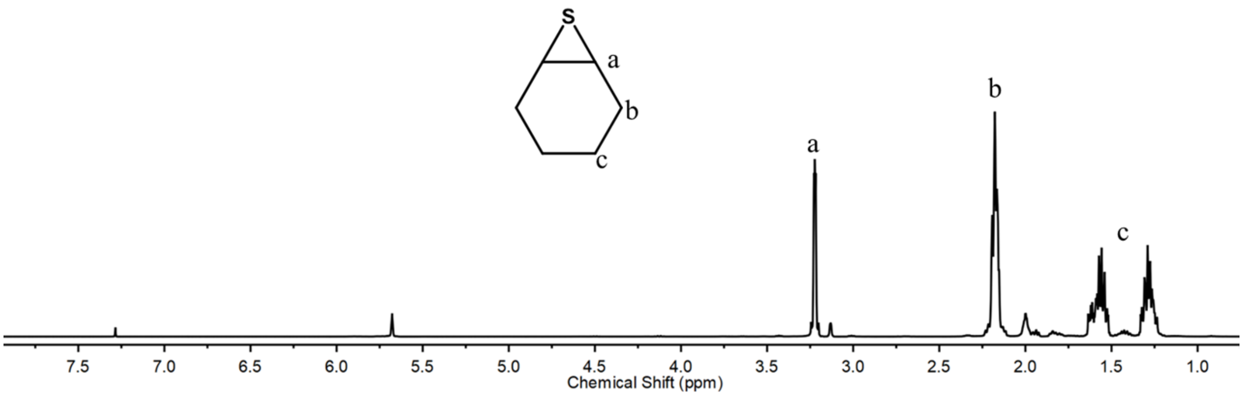


Figure S7. ^1H NMR spectrum of CHS in $CDCl_3$.

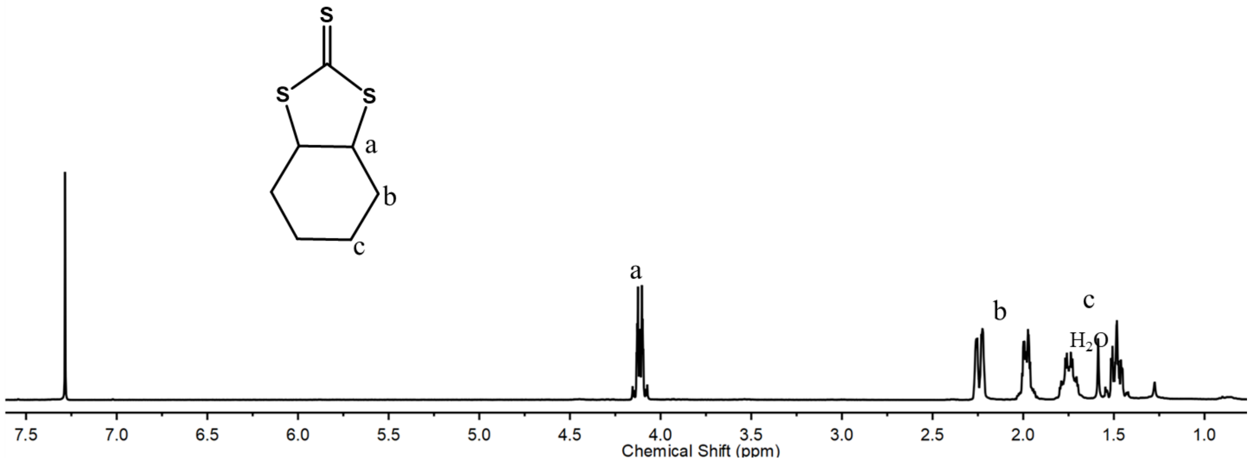


Figure S8. ^{1}H NMR spectrum of CHS based cyclic trithiocarbonate in $CDCl_3$.

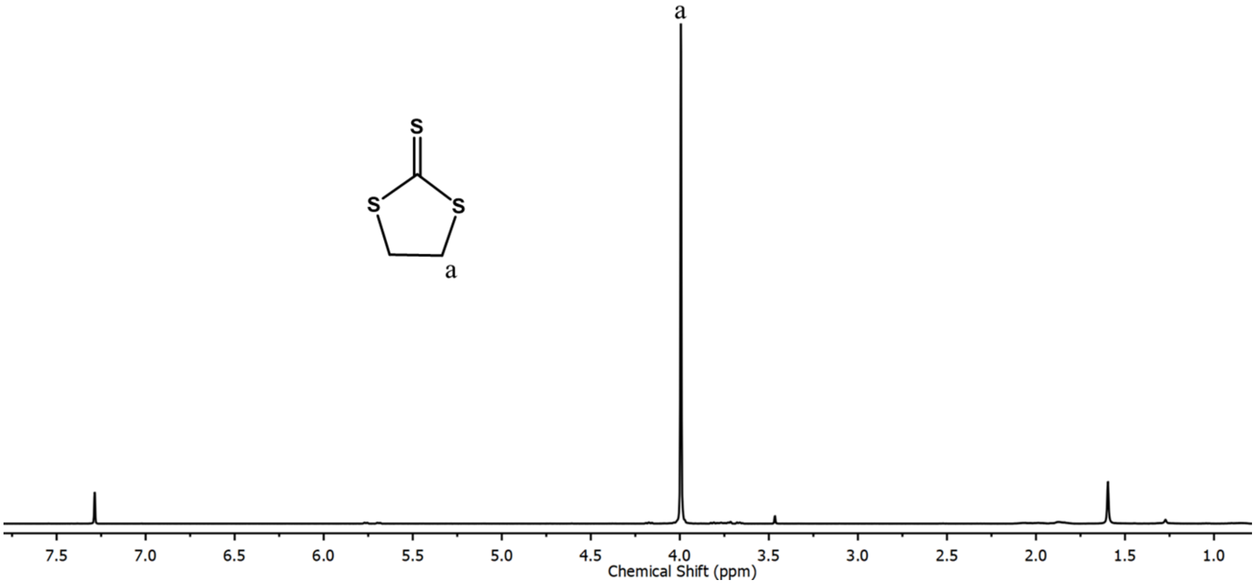


Figure S9. ^{1}H NMR spectrum of ES based cyclic trithiocarbonate in $CDCl_3$.

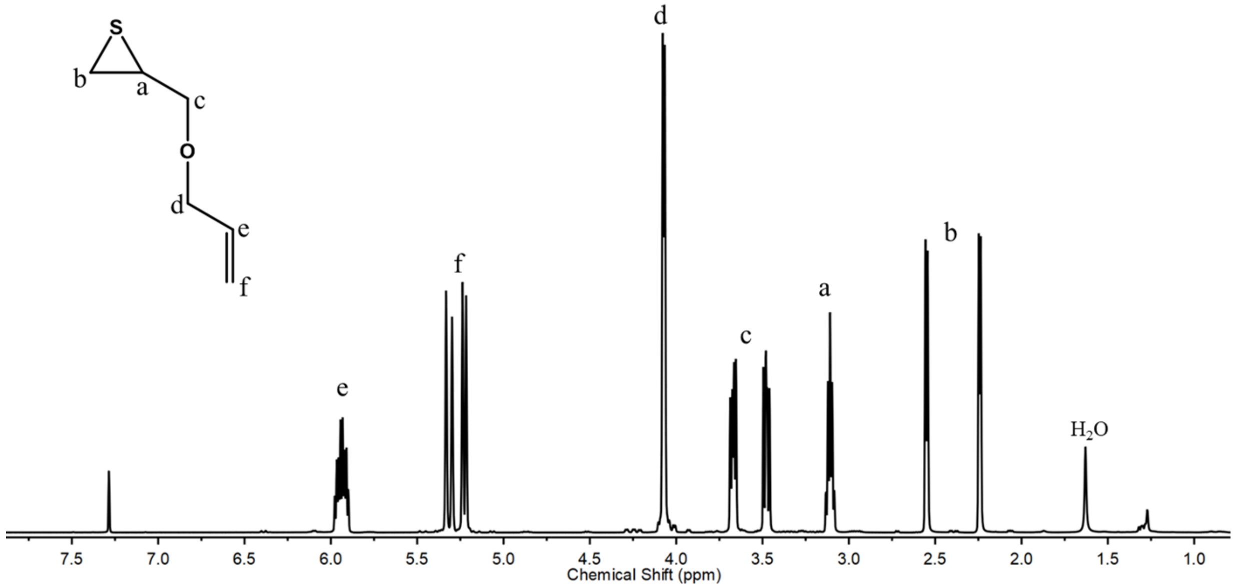


Figure S10. ^{1}H NMR spectrum of AES in CDCl$_3$.

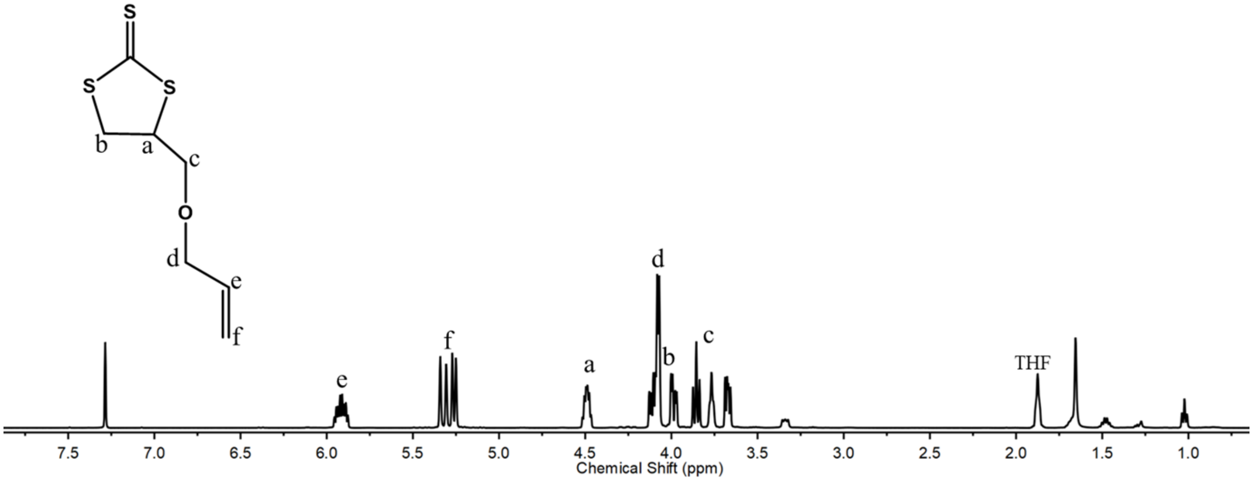


Figure S11. ^{1}H NMR spectrum of AES based cyclic trithiocarbonate in CDCl$_3$.

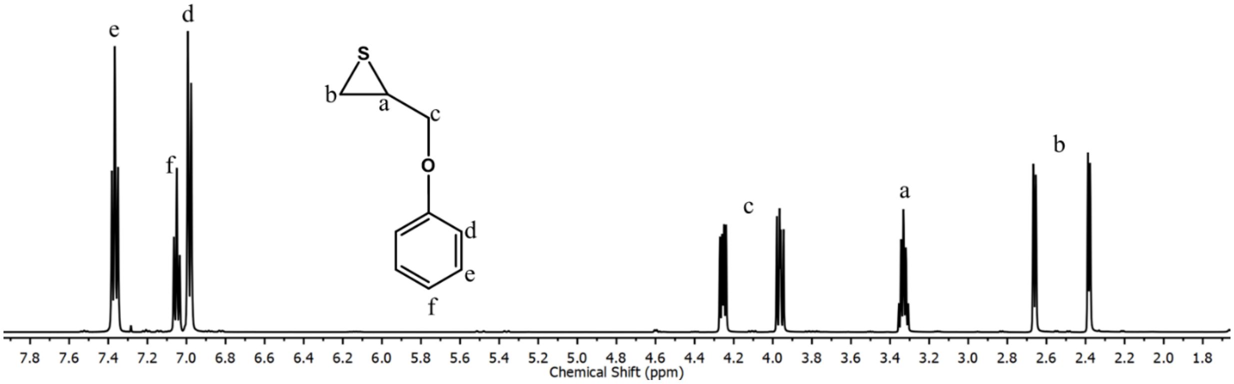


Figure S12. ^{1}H NMR spectrum of PES in $CDCl_3$.

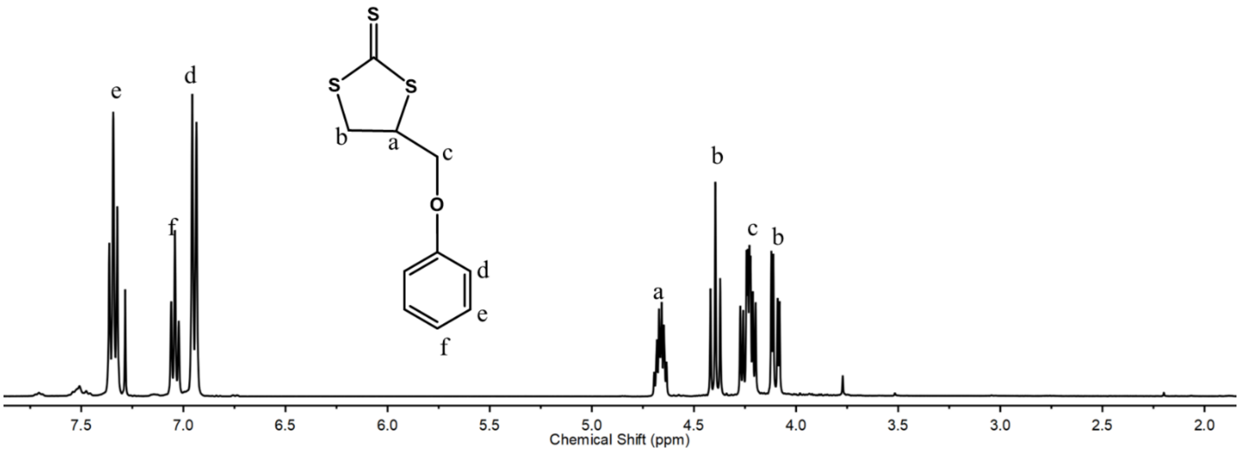


Figure S13. ^{1}H NMR spectrum of PES based cyclic trithiocarbonate in $CDCl_3$.

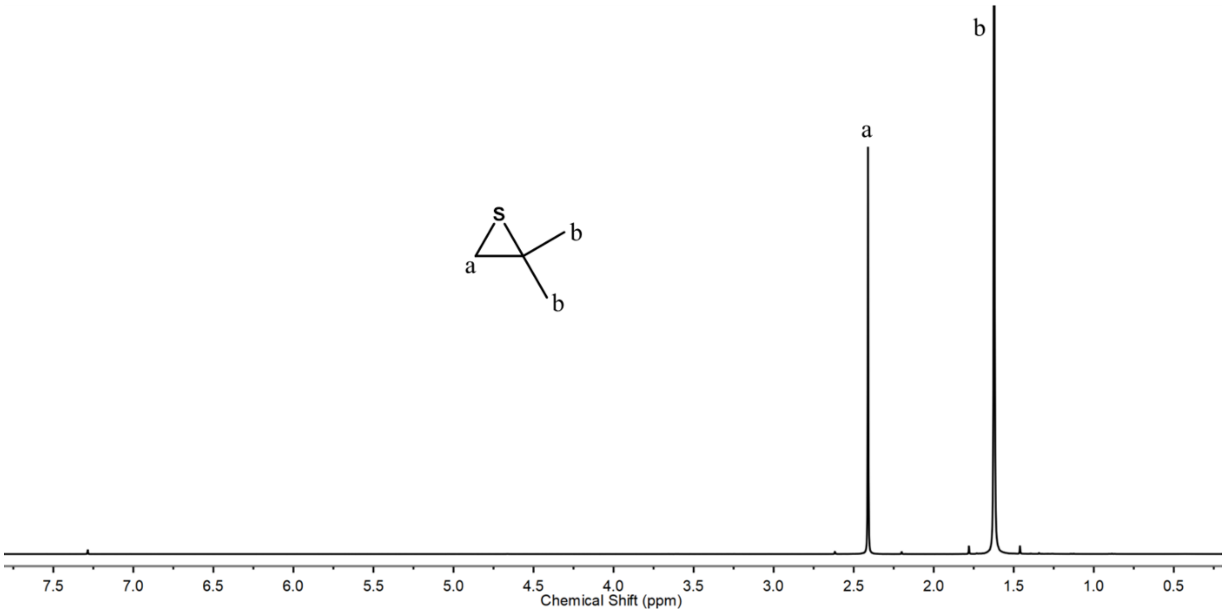


Figure S14. ^{1}H NMR spectrum of iBS in $CDCl_3$.

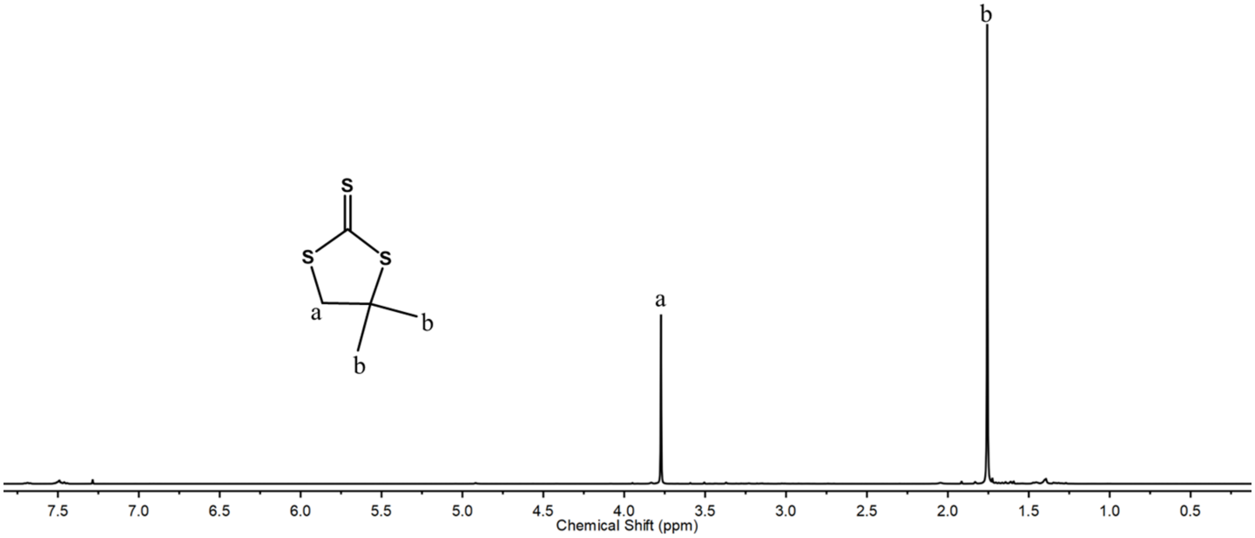


Figure S15. ^{1}H NMR spectrum of iBS based cyclic trithiocarbonate in $CDCl_3$.

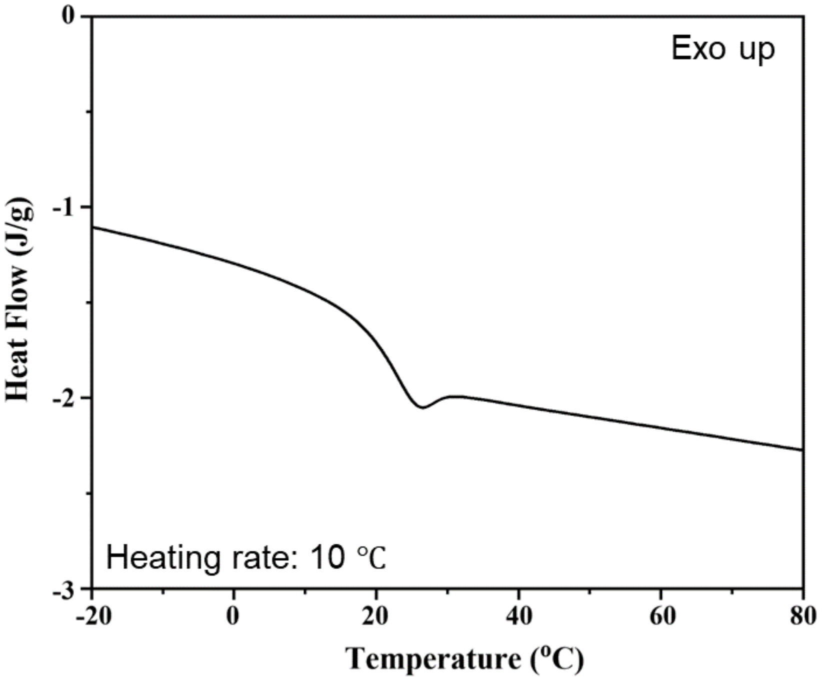


Figure S16. DSC curve for the PPSC under N_2.

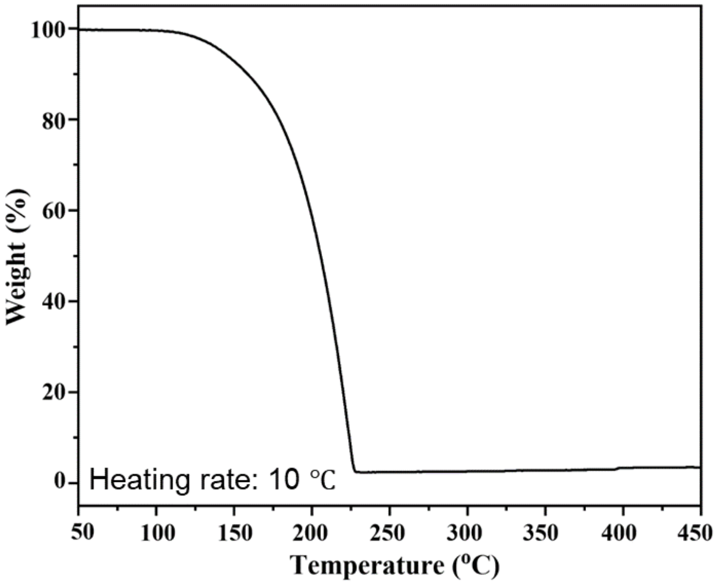


Figure S17. TGA curve for the PPSC under N_2.

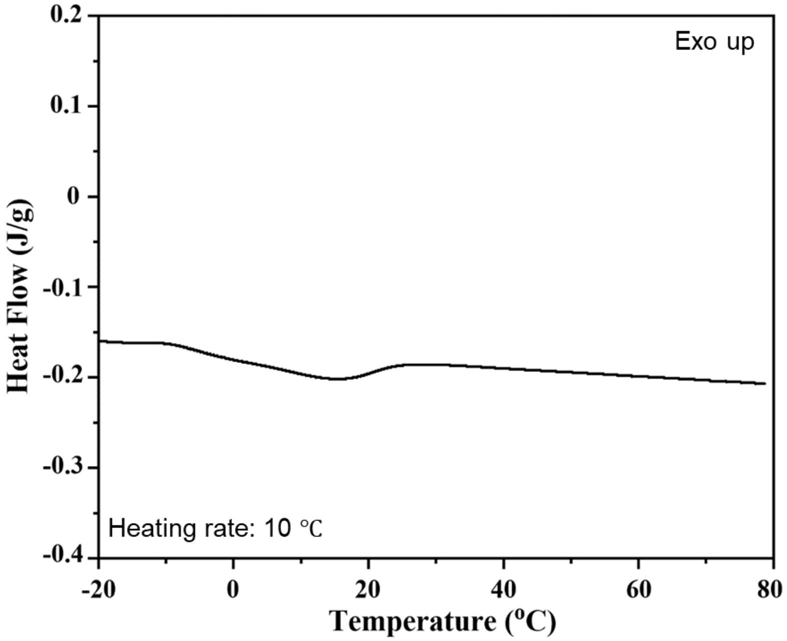


Figure S18. DSC curve for the PESC under N_2.

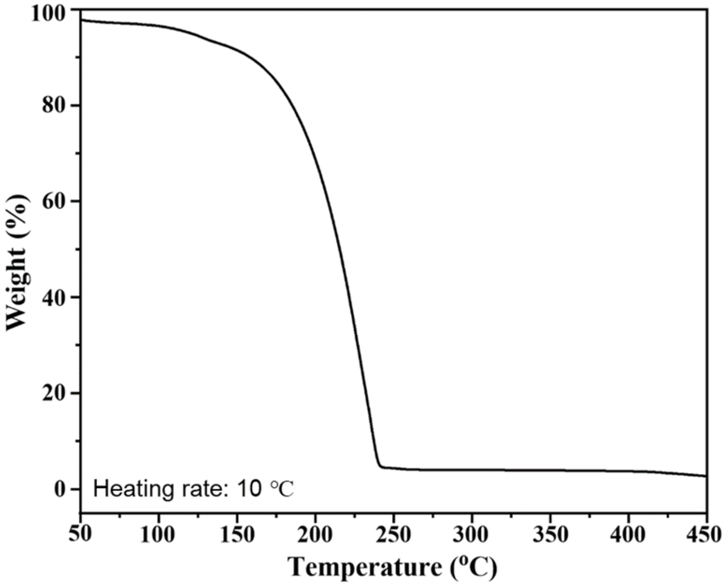


Figure S19. TGA curve for the PESC under N_2.

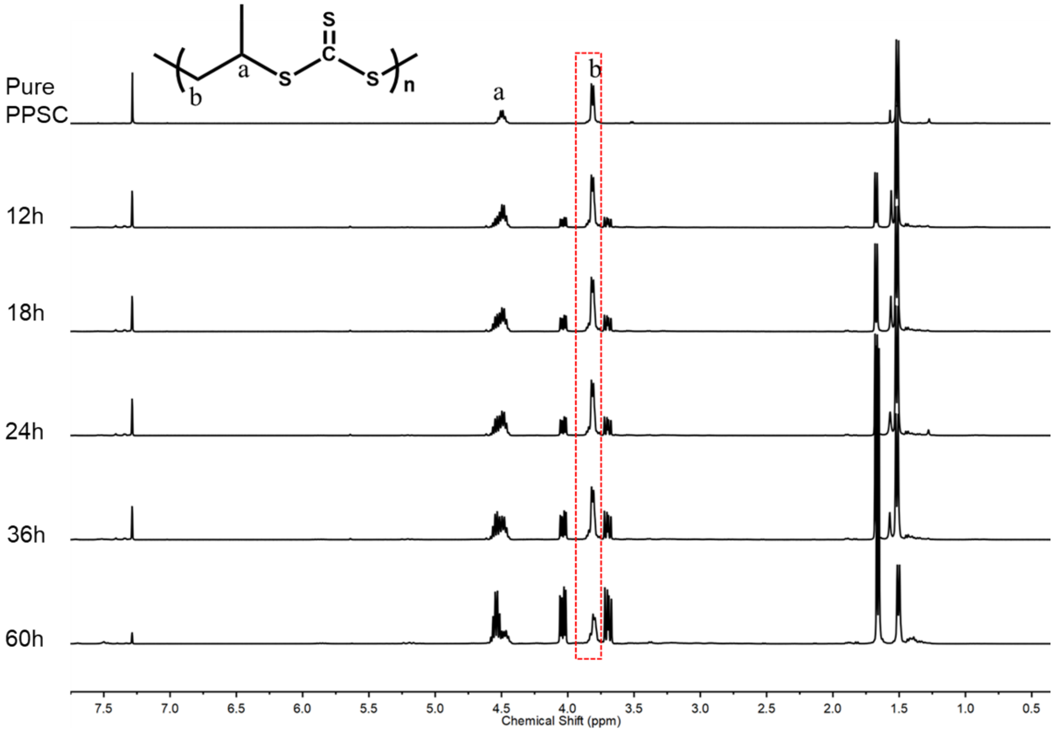


Figure S20. ^{1}H NMR spectra of the linear poly(trithiocarbonate) treated with UV at different times.

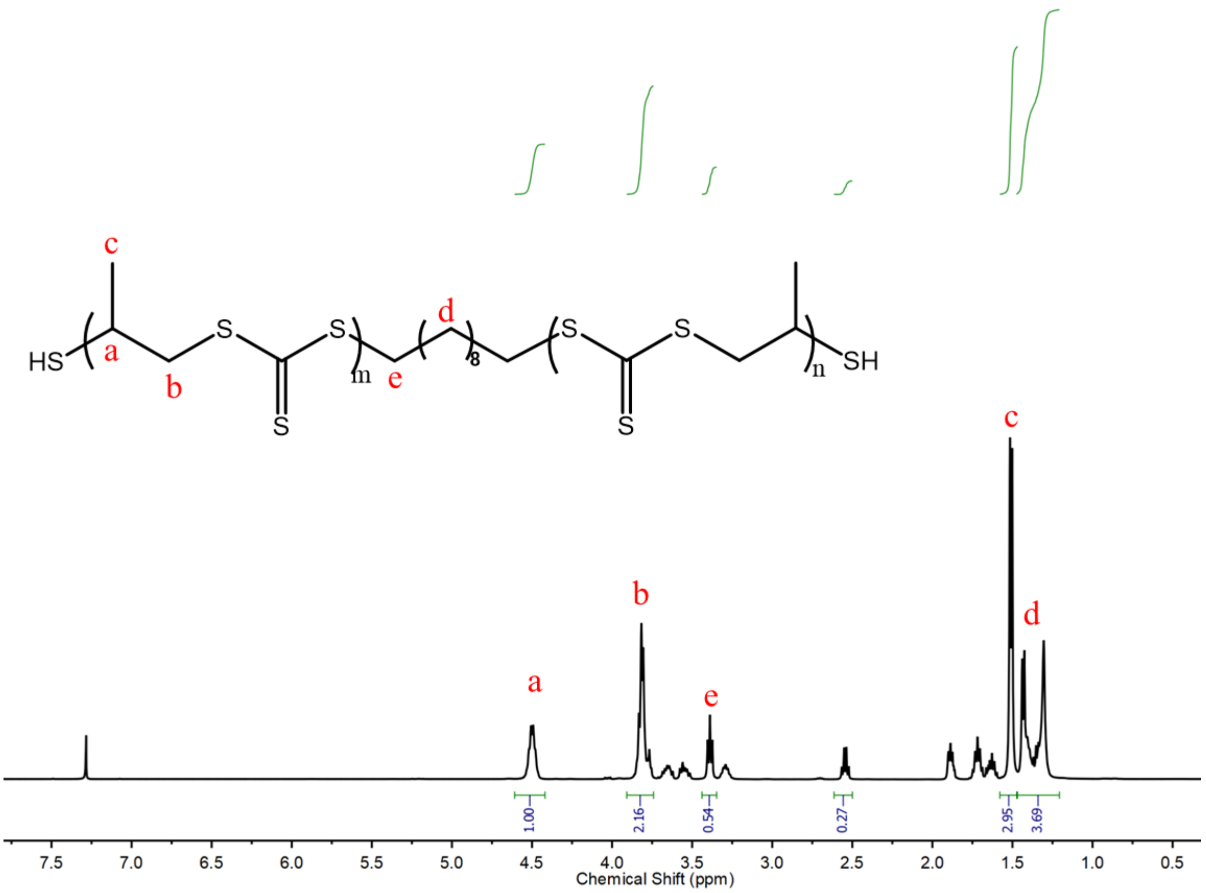


Figure S21. ^{1}H NMR spectrum of the low molar mass poly(trithiocarbonate)s synthesized using 1,10-decanedithiol as chain transfer agent.

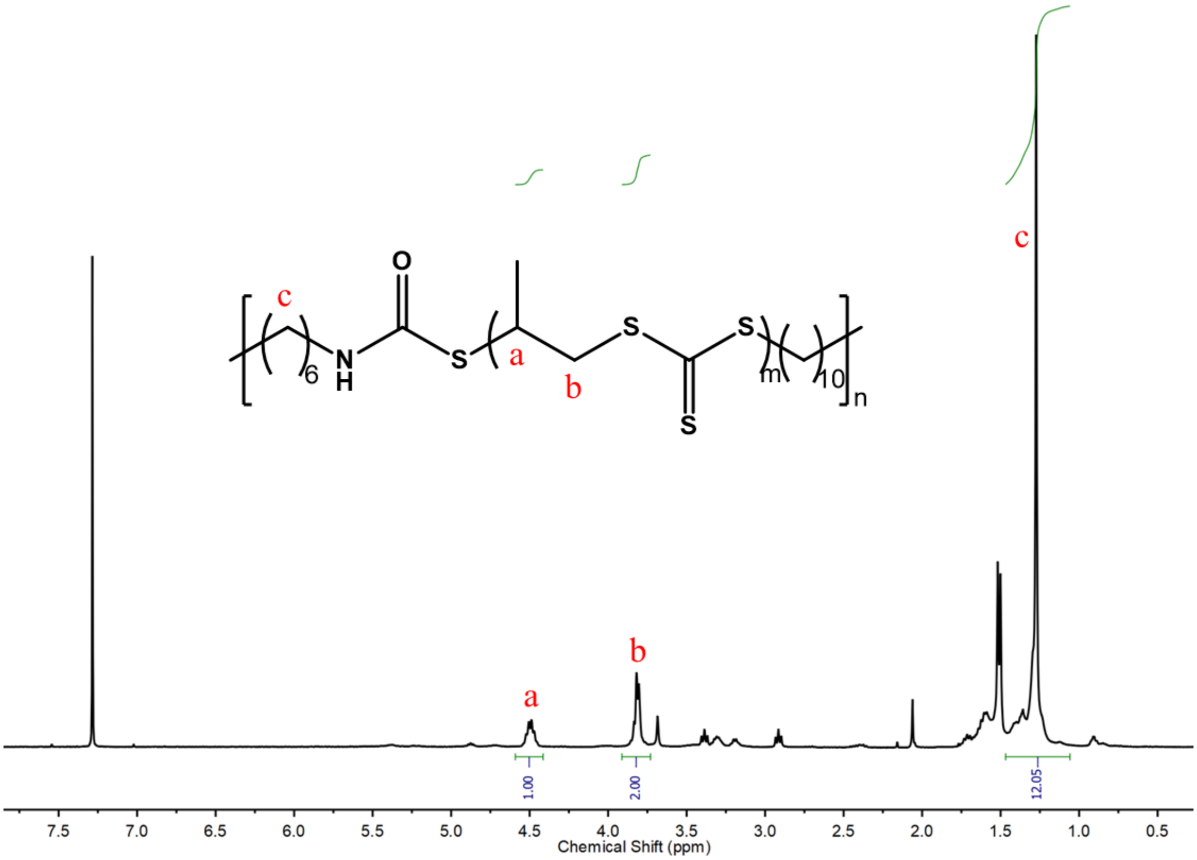


Figure S22. ^{1}H NMR spectrum of degradable polyethylene synthesized by polycondensation of poly(trithiocarbonate)s with hexamethylene diisocyanate**.**

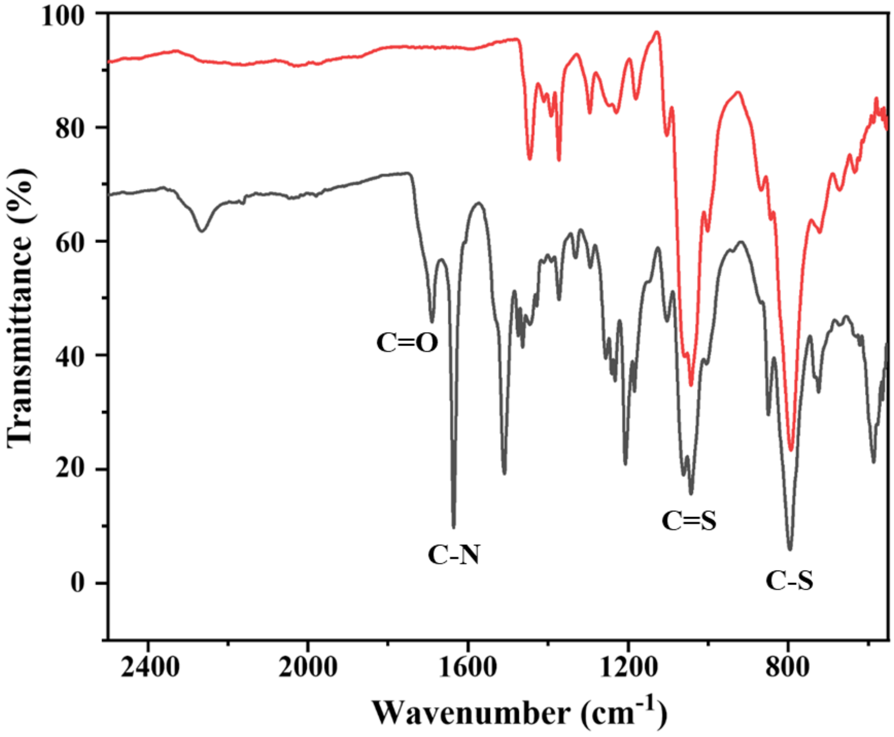


Figure S23. FTIR spectra of the poly(trithiocarbonate) (red) and poly(thiourethane) (black).

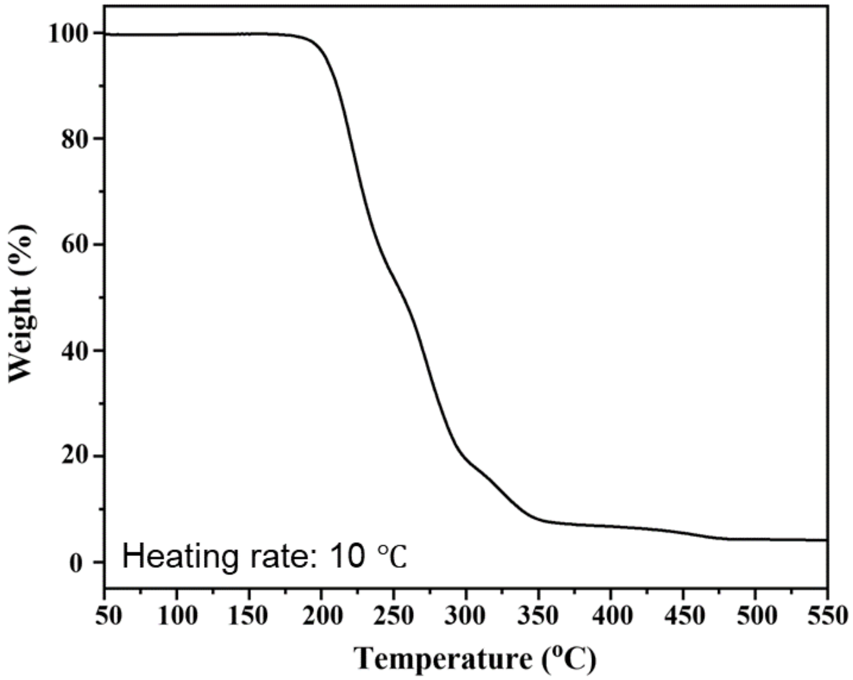


Figure S24. TGA curve for the poly(thiourethane) under N_2.

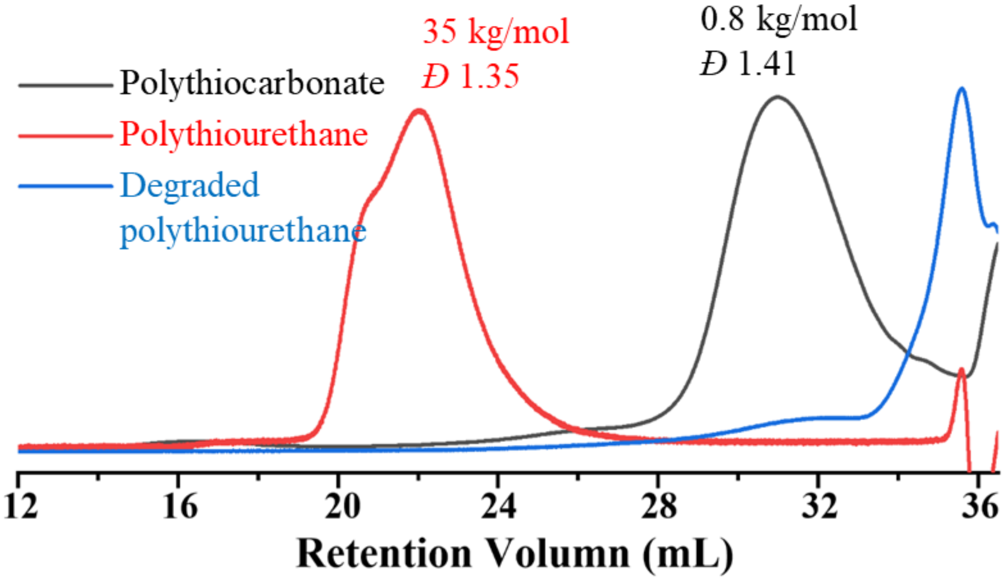


Figure S25. SEC traces of low molar mass poly(trithiocarbonate), poly(thiourethane) and degraded poly(thiourethane).