Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting information:

Polymers from sugars and CS_2: ring opening Copolymerisation of a ᴅ-xylose anhydrosugar oxetane

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1 Materials and Methods

All manipulations were performed under an atmosphere of argon using standard Schlenk techniques unless otherwise stated. (*R*,*R*)-1,2-Cyclohexanediamino-N,N'bis(3,5-di-t-butylsalicyilidene)chromium(III) (CrSalen) was purchased from Sigma Aldrich and used without further purification. Bis(triphenylphosphine)iminium chloride (PPNCl) was singly recrystallized from anhydrous acetonitrile prior to use. Anhydrous ortho-dichlorobenzene, acetonitrile, DCM and THF were purchased from Sigma Aldrich. All other reagents were purchased from either Sigma Aldrich, Alfa Aesar or Acros Organics and used without further purification. All solvents used were anhydrous unless otherwise stated. **1** was synthesised in three steps from D-xylose according to previous reports (51% overall yield).[1, 2] **2** characterisation data matched previous reports.[3]

^{1}H and ^{13}C{^{1}H} NMR spectra were recorded on a Bruker 400 or 500 MHz instrument and referenced to residual solvent peaks. Coupling constants are given in Hertz. Polymer conversions were determined by ^{1}H NMR spectroscopy. **End group titration by ^{31}P NMR spectroscopy** followed a procedure from the literature,[4] with a 10s T1 delay**.**

Mass spectrometry measurements were recorded with a microToF electrospray time-of-flight (ESI-ToF) mass spectrometer (Bruker Daltonik) in acetonitrile.

Size-exclusion chromatography (SEC) was carried out using either a THF or DMF eluent. Multi analysis software was used to process the data. Polymer samples were dissolved at a concentration of 2 mg mL^{-1}.
THF samples were recorded on an Agilent 1260 Infinity series instrument at 1 mL min^{-1} at 35 °C using two PLgel 5 µm MIXED-D 300 × 7.5 mm columns in series. Samples were detected with a differential refractive index (RI) detector. Number-average molecular weight ($M_{n,SEC}$), and dispersities, ($Đ_M$ (M_w/M_n)) were calculated against a polystyrene calibration (11 polystyrene standards of narrow molecular weight, ranging from M_w 615 – 568000 Da).

Differential scanning calorimetry (DSC) was carried out using using a MicroSC multicell calorimeter from Setaram. The measurement cell and the reference cell were both a 1 mL Hastelloy C cell; a mass of 3–6 mg of polymeric material was loaded into the measurement cell with the reference cell empty. The experiment was performed under nitrogen gas and the sample heated and cooled at a rate of 20 K min^{-1}. A second heating and cooling cycle was carried out immediately following completion of the first. Glass transition (T_g's) are reported from the second heating cycle unless otherwise stated. The Calisto program was employed to collect and process the data. Data was plotted using Origin 2018.

Thermogravimetric analysis (TGA) was conducted on a A Setsys Evolution TGA 16/18 from Setaram. The sample was loaded into a 170 µL alumina crucible and the analytical chamber purged with argon (200 mL min^{-1}) for 40 min prior to starting the analysis. The sample was then heated under an argon flow (20 mL min^{-1}) from 30 to 600 °C at a rate of 2 ˚C min^{-1}. The mass spectrometer was an Omnistar GSD 320 by Pfeiffer Vacuum, equipped with a quadrupole mass analyser and a SEM detector. The Calisto program was employed to collect and process the data. Data was plotted using Origin 2018.

Wide-angle X-ray scattering (WAXS) analysis was performed on a SAXSpoint 2.0 by Anton Paar, equipped with a microfocus X-ray source (Cu, 50 W) and a EIGER R 1M detector. Ground samples were held in place by tape and loaded onto a multi-solid sampler mounted on a vario-stage sample-holder. Two frames of 30 minutes each were collected with only one frame reported for each sample with the tape background subtracted. Data was processed using SAXSAnalysis processing software by Anton Paar and plotted in Origin 2018.

Photoreactors: All batch photoreactions were conducted in commercially-available EvoluChemPhotoRedOx Box reactors purchased from HepatoChem Inc.(100 Cummings Center, Suite 451C, Beverly, MA 01915 USA). The light source employed in this work was a 365DX LED (λ = 365 nm; 25 mW/cm^2), purchased from HepatoChem Inc.

2 General Procedures

2.1 General procedure 1/CS_2 ROCOP

Under an argon atmosphere, **CrSalen** (40 µL, 0.125 mol L^{-1} solution in anhydrous THF, 1 x 10^{-2} mmol, 1.00 equiv.), PPNCl (20 µL, 0.25 mol L^{-1} solution in anhydrous DCM , 1 x 10^{-2} mmol, 1.00 equiv.) and CS_2 (242 µL, 4.00 mmol, 400.00 equiv.) were added to a 1.34 mol L^{-1} σ-dichlorobenzene solution of oxetane **1** (344 mg, 2.00 mmol, 200.00 equiv.). The vessel was heated to 80 °C. The reaction progress was monitored by ^1H NMR spectroscopy and SEC. Once stirring had stopped, the reaction was terminated by cooling the reaction vessel down. The resultant sticky solid was dissolved in $CHCl_3$ before precipitation of the polymer with cold hexane. The suspension was then centrifuged (3000 rpm, 5 minutes), the solid collected and dried *in vacuo* at 100 °C to yield poly(**CS_2**-*co*-**1**) (322 mg, 65% yield).

2.2 General procedure for 1/CS_2 cycloaddition

Under an argon atmosphere, **CrSalen** (40 µL, 0.125 mol L^{-1} solution in anhydrous THF, 1 x 10^{-2} mmol, 1.00 equiv.), PPNCl (20 µL, 0.25 mol L^{-1} solution in anhydrous DCM, 1 x 10^{-2} mmol, 1.00 equiv.) and CS_2 (242 µL, 4.00 mmol, 400.00 equiv.) were added to a 0.67 mol L^{-1} σ-dichlorobenzene solution of oxetane **1** (344 mg, 2.00 mmol, 200.00 equiv.). The vessel was heated to 110 °C. After 20 h, the reaction was quenched by cooling down to room temperature. The crude reaction mixture was immediately subjected to column chromatography (DCM eluent, 5 cm diameter column, 60 g silica, product eluted in 200–750 mL). The solvent was removed *in vacuo* at 40 °C to yield monomer-grade xanthate **2** as fine yellow crystals (297 mg, 60% yield, R_f (DCM) = 0.43).

2.3 General procedure for kinetic ROCOP experiments

Under an argon atmosphere, **CrSalen** (40 µL, 0.125 mol L^{-1} solution in anhydrous THF, 1 x 10^{-2} mmol, 1.00 equiv.), PPNCl (20 µL, 0.25 mol L^{-1} solution in anhydrous DCM , 1 x 10^{-2} mmol, 1.00 equiv.), and CS_2 (242 µL, 4.00 mmol, 400.00 equiv.) were added to a σ-dichlorobenzene solution of oxetane **1** (344 mg, 2.00 mmol, 200.00 equiv.) with *para*-xylene as an internal standard(100 µL). The total concentration of the mixture was 1.34 mol L^{-1}. The reaction mixture was divided in approximately equal amounts into air and vacuum tight polymerisation tubes. The vessels were then heated at 80 °C. At pre-determined intervals, the reaction vessels were taken off the heat and the polymerisation quenched with a few drops of benzoic acid solution (10 mg/mL). Aliquots of the quenched solutions were then subjected to ^1H NMR spectroscopy and SEC analysis.

2.4 Depolymerisation of poly(CS_2-*co*-1)

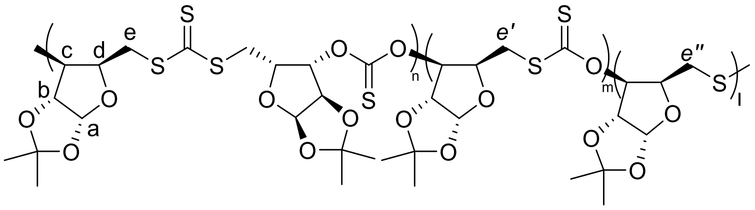
Under an argon atmosphere, **CrSalen** (10 µL, 0.125 mol L^{-1} solution in anhydrous THF, 1 x 10^{-2} mmol, 1.00 equiv.) and PPNCl (10 µL, 0.125 mol L^{-1} solution in anhydrous DCM , 1 x 10^{-2} mmol, 1.00 equiv.) were added to a 1.34 mol L^{-1} σ-dichlorobenzene solution of poly(**CS_2**-*co*-**1**) (248 mg, 1.00 mmol, 200.00 equiv.).The vessel was heated to 110 °C. After 20 h, the reaction was terminated by cooling the reaction vessel down. ^1H NMR spectroscopy and SEC analysis was carried out on the crude reaction mixture to determine the percentage of depolymerisation.

2.5 Degradation of poly(CS_2-*co*-1) under UV light

Under an argon atmosphere, tris(trimethylsilyl)silane (0.226 g, 0.91 mmol, 7.5 monomer equiv.) was added to a THF solution (4.5 mL) of poly(**CS_2**-*co*-**1**) (0.030 g, 0.12 mmol, 1 monomer equiv.). The solution was divided equally between 7 vacuum-tight vials. The vials were placed under UV light (λ = 365 nm) and taken off at predetermined intervals. All crude reaction mixtures were then subjected to ^{1}H NMR spectroscopy and SEC analysis.

Degradation in the absence of silane is identical to the procedure described above without addition of tris(trimethylsilyl)silane.

3 NMR characterisation of poly(CS_2-*co*-1)



n:m:l = 74:12:14

poly(CS_2-*co*-1)
Yellow powder, 60% yield (150 mg).

^{1}H NMR (400 MHz, CDCl$_3$) δ 5.95 (d, *J* = 3.8 Hz, 1H, $\boldsymbol{H_a}$), 5.62 (d, *J* = 2.9 Hz, 1H, $\boldsymbol{H_c}$), 4.69 (d, *J* = 3.9 Hz, 1H, $\boldsymbol{H_b}$), 4.61 (td, *J* = 6.8, 3.0 Hz, 1H, $\boldsymbol{H_d}$), 3.79 – 3.61 (m, 2H, $\boldsymbol{H_e}$), 3.55 – 3.44 (m, 1/4H, $\boldsymbol{H_{e'}}$), 3.10 – 2.66 (m, 1/4H, $\boldsymbol{H_{e''}}$), 1.60 – 1.47 (m, 3H, $\boldsymbol{H_f}$), 1.44 – 1.28 (m, 3H, $\boldsymbol{H_f}$).

^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$) δ 222.5 (SC(S)S), 193.0 (OC(S)O), 112.7 ($\boldsymbol{C_{acetal}}$), 104.9 ($\boldsymbol{C_a}$), 85.2 ($\boldsymbol{C_c}$), 83.2 ($\boldsymbol{C_b}$), 76.8 ($\boldsymbol{C_d}$), 34.5 ($\boldsymbol{C_e}$), 26.8 ($\boldsymbol{C_f}$), 26.5 ($\boldsymbol{C_f}$).

$M_{n,SEC}$ = 14400 g mol^{-1}, $Đ_m$ = 1.27; T_g = 137 °C; $T_{d,onset}$ = 208 °C.

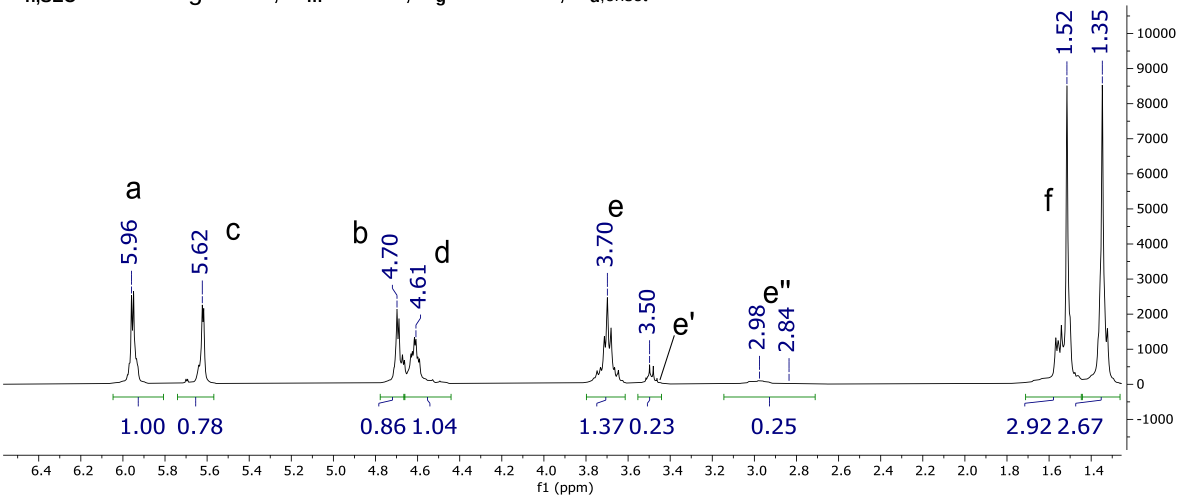


Fig. S1. ^{1}H NMR spectrum (CDCl$_3$) of poly(**CS_2**-*co*-**1**).

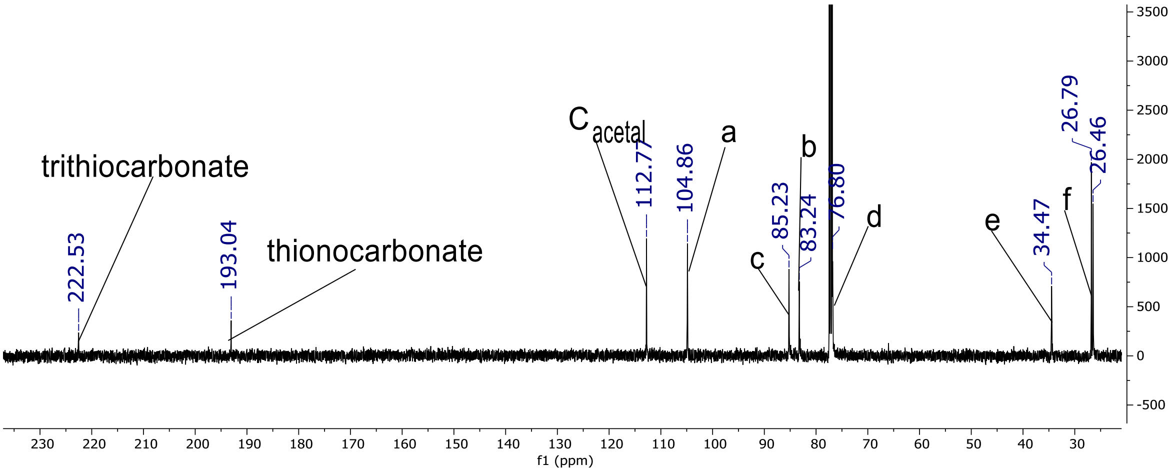


Fig. S2. ^{13}C{^{1}H} NMR spectrum (CDCl$_3$) of poly(**CS_2**-*co*-**1**). (CHCl$_3$ residual signal at 77.2 ppm).

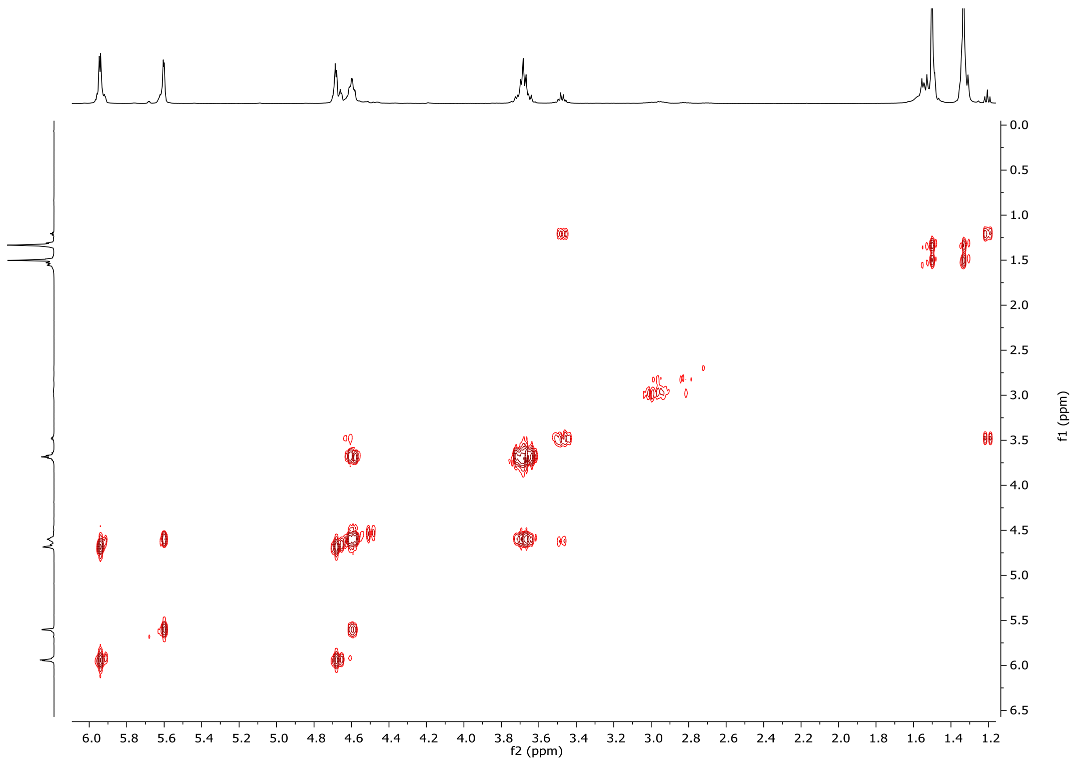


Fig. S3. ^{1}H COSY NMR (CDCl$_3$) of poly(**CS$_2$**-*co*-**1**).

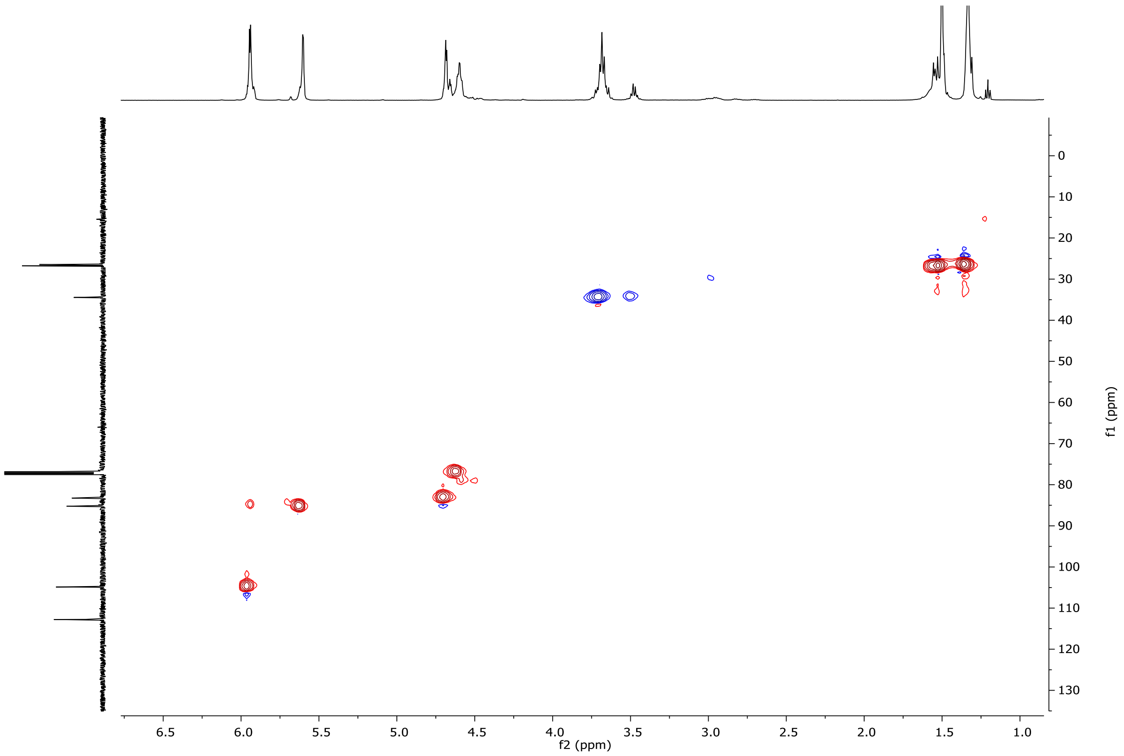


Fig. S4. ^{1}H-^{13}C{^{1}H} HSQC NMR (CDCl$_3$) of poly(**CS$_2$**-*co*-**1**).

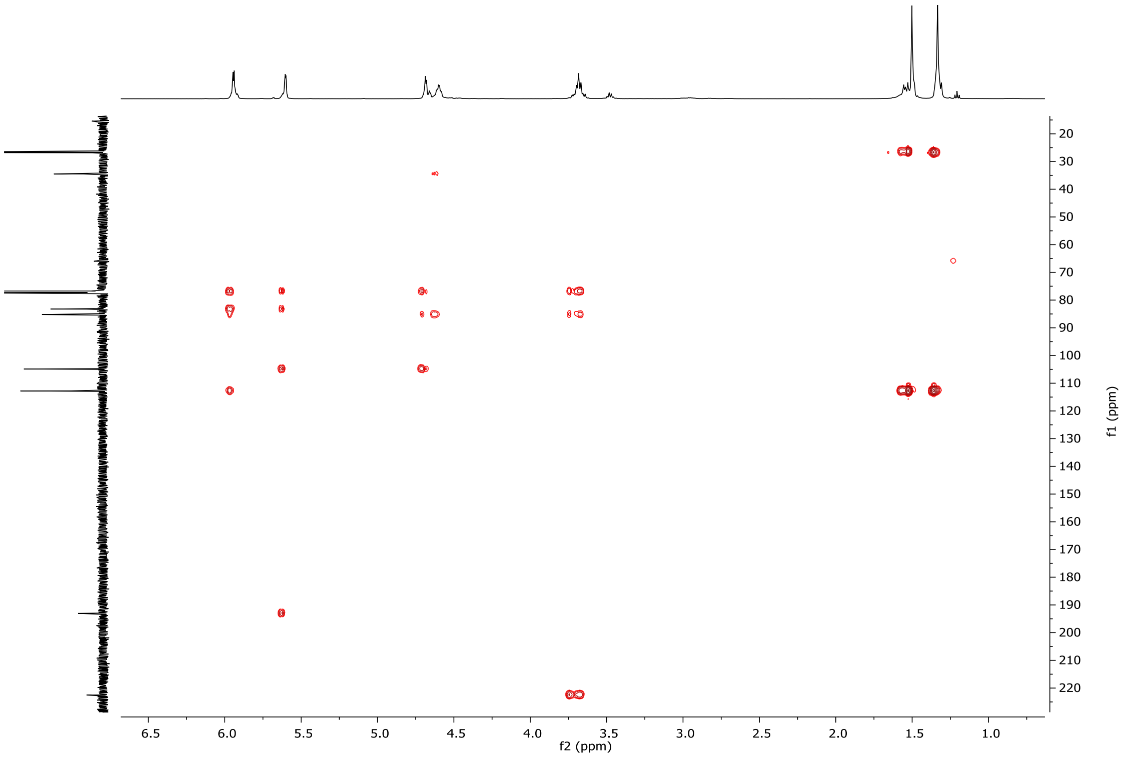


Fig. S5. ^{1}H-^{13}C{^{1}H} HMBC NMR (CDCl$_3$) of poly(**CS$_2$**-*co*-**1**).

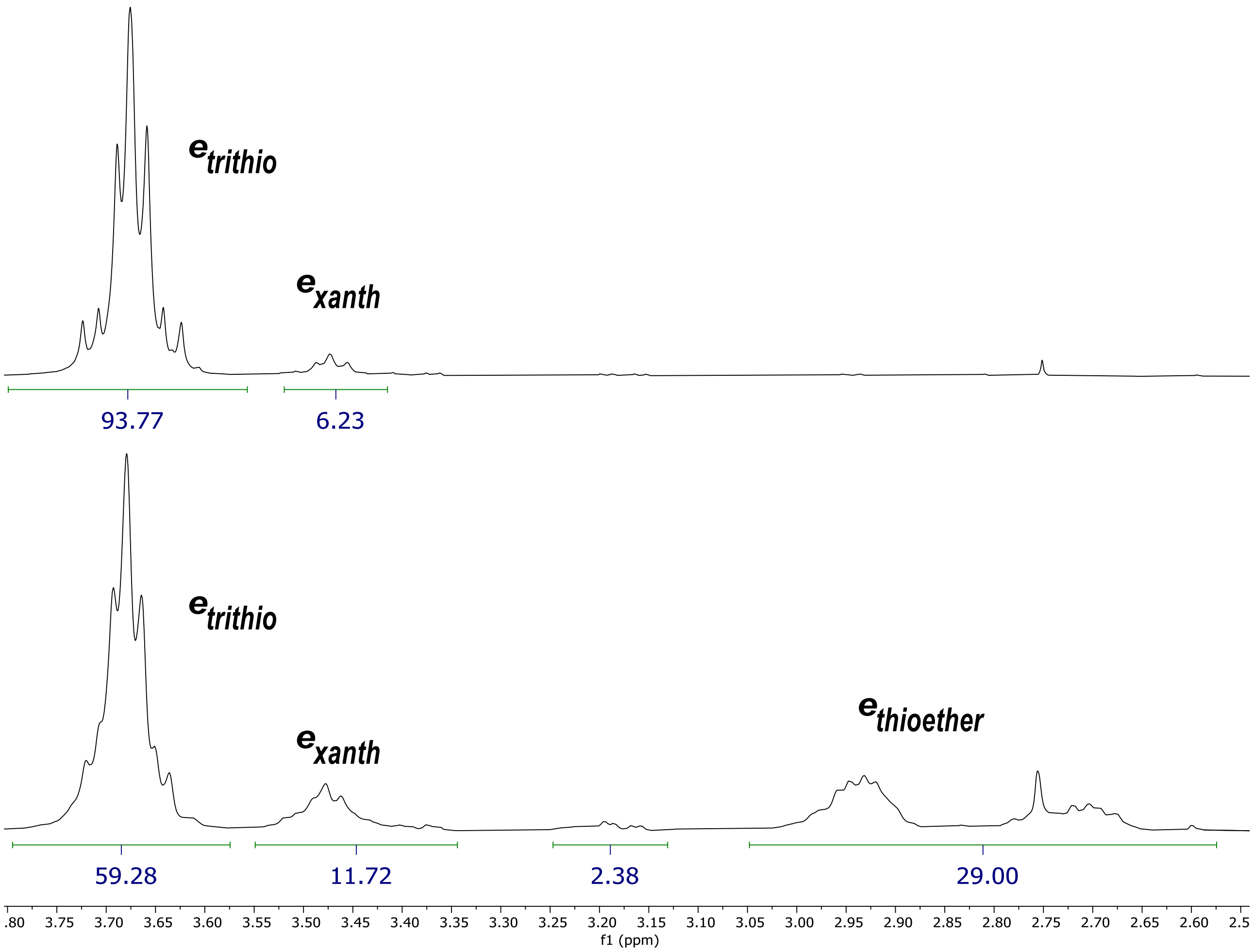


Fig. S6. ^{1}H NMR (CDCl$_3$) spectra of 94% alternating poly(**CS$_2$**-*co*-**1**) (top) and 59% alternating poly(**CS$_2$**-*co*-**1**) (bottom).

4 Thermal characterisation of poly(CS_2-*co*-1) with varying alternating trithio/thionocarbonate linkages

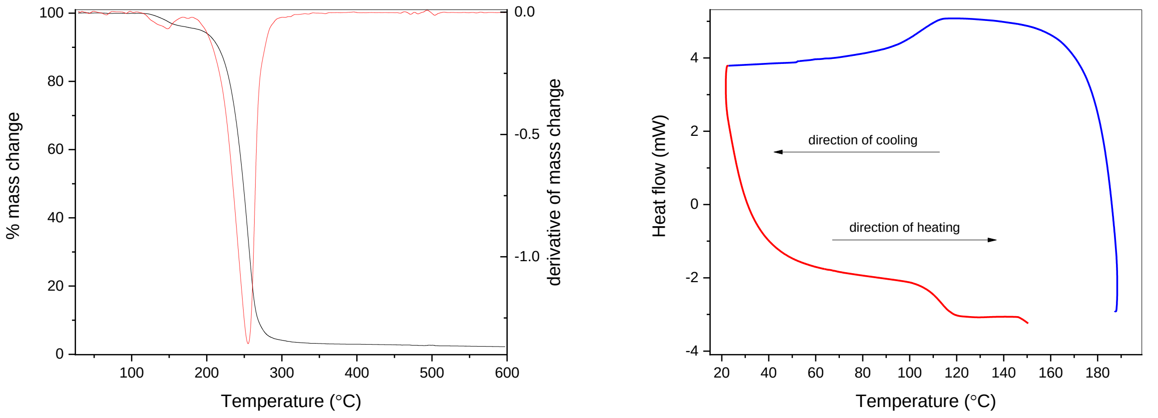


Fig. S7. (left) TGA (black = % mass loss, red = derivative of % mass loss) and (right) DSC (first cooling and second heating cycles) traces of 95% alternating trithio/thionocarbonate poly(**CS_2**-*co*-**1**) (Table 3, entry 1, $M_{n,SEC}$ = 14000 g mol^{-1}, $Đ_M$ =1.71; T_g = 114 °C; $T_{d,onset}$ = 188 °C; T_{d5} = 216°C; $T_{d,max}$= 255 °C with 7% char remaining at 600 °C) measured under argon.

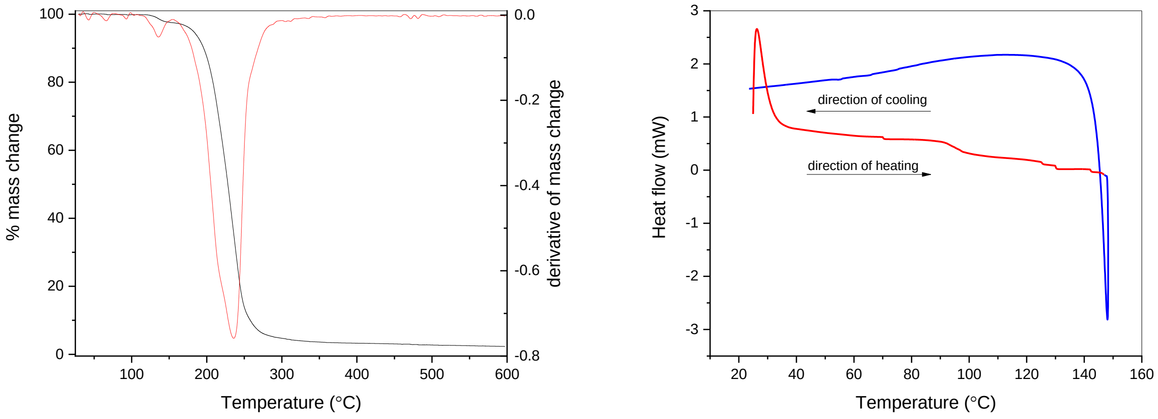


Fig. S8.(left) TGA (black = % mass loss, red = derivative of % mass loss) and (right) DSC (first cooling and first heating cycles) traces of 89% alternating trithio/thionocarbonate poly(**CS_2**-*co*-**1**) (Table 3, entry 2, $M_{n,SEC}$ = 15400 g mol^{-1}, $Đ_M$ =2.13; T_g = 110 °C; $T_{d,onset}$ = 167 °C; T_{d5} = 190°C; $T_{d,max}$= 236 °C with 5% char remaining at 600 °C) measured under argon.

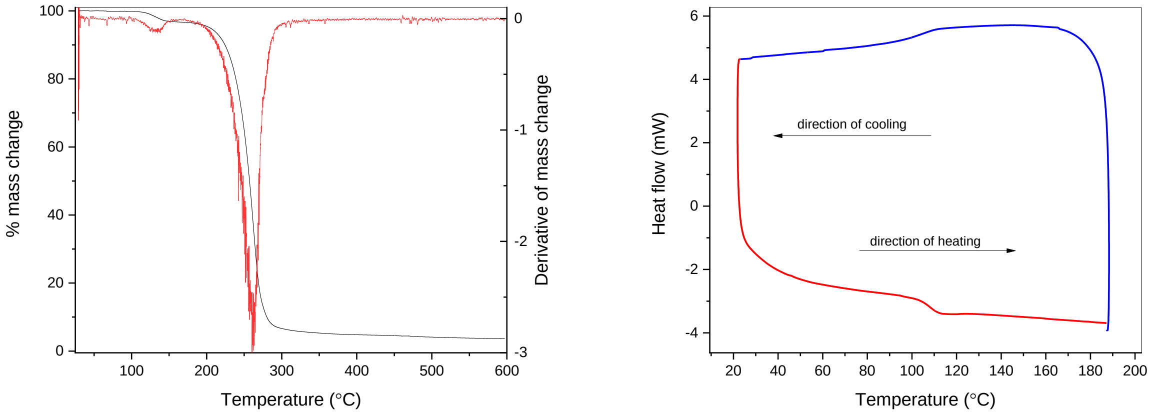


Fig. S9. (left) TGA (black = % mass loss, red = derivative of % mass loss) and (right) DSC (first cooling and first heating cycles) traces of 87% alternating trithio/thionocarbonate poly(**CS_2**-*co*-**1**) (Table 3, entry 3, $M_{n,SEC}$ = 9100 g mol^{-1}, $Đ_M$ =1.78; T_g = 108 °C; $T_{d,onset}$ = 191 °C; T_{d5} = 216 °C; $T_{d,max}$= 262 °C with 8% char remaining at 600 °C) measured under argon.

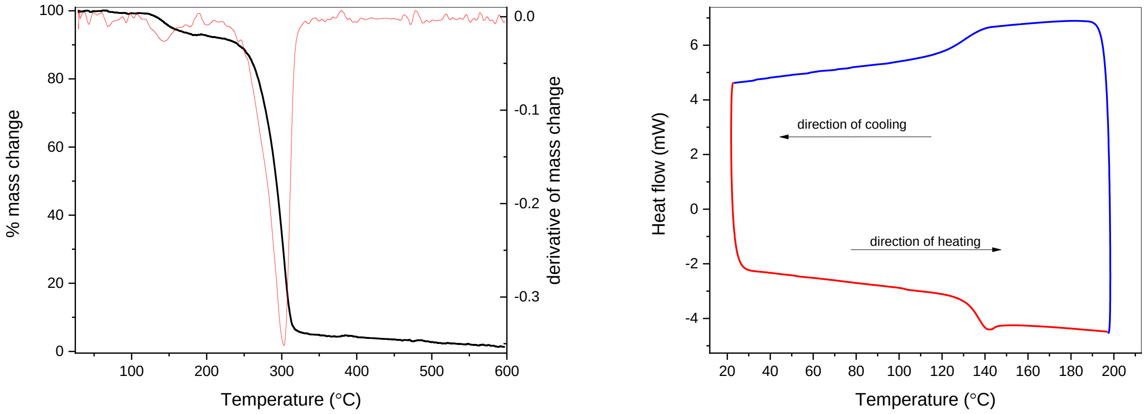


Fig. S10. (left) TGA (black = % mass loss, red = derivative of % mass loss) and (right) DSC (first cooling and first heating cycles) traces of 69% alternating trithio/thionocarbonate poly(**CS_2**-*co*-**1**) (Table 3, entry 4, $M_{n,SEC}$ = 14400 g mol^{-1}, $Đ_M$ =1.27; T_g = 137 °C; $T_{d,onset}$ = 208 °C; T_{d5} = 257 °C; $T_{d,max}$= 304 °C with 10% char remaining at 600 °C) measured under argon.

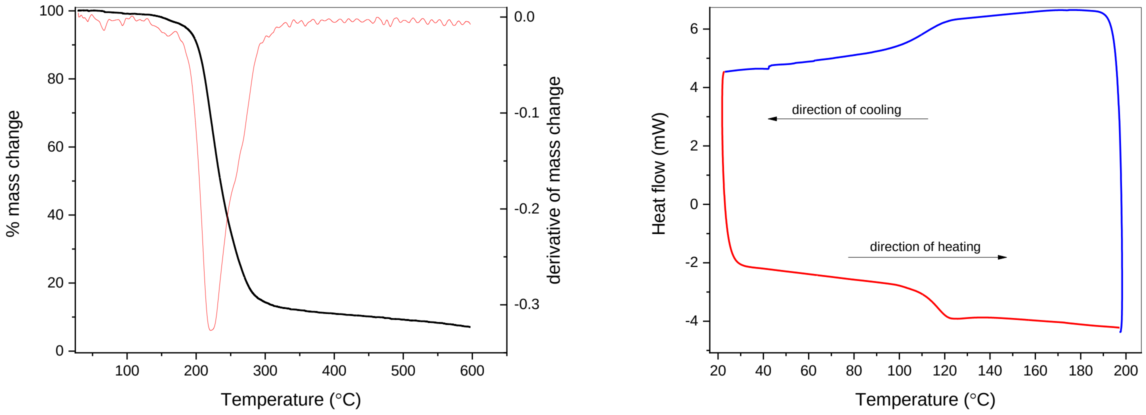


Fig. S11. (left) TGA (black = % mass loss, red = derivative of % mass loss) and (right) DSC (first cooling and first heating cycles) traces of 61% alternating trithio/thionocarbonate poly(**CS$_2$**-*co*-**1**) (Table 3, entry 5, $M_{n,SEC}$ = 14000 g mol^{-1}, $Đ_M$ =1.19; T_g = 117 °C; $T_{d,onset}$ = 172 °C; T_{d5} = 186 °C; $T_{d,max}$= 221 °C with 12% char remaining at 600 °C) measured under argon.

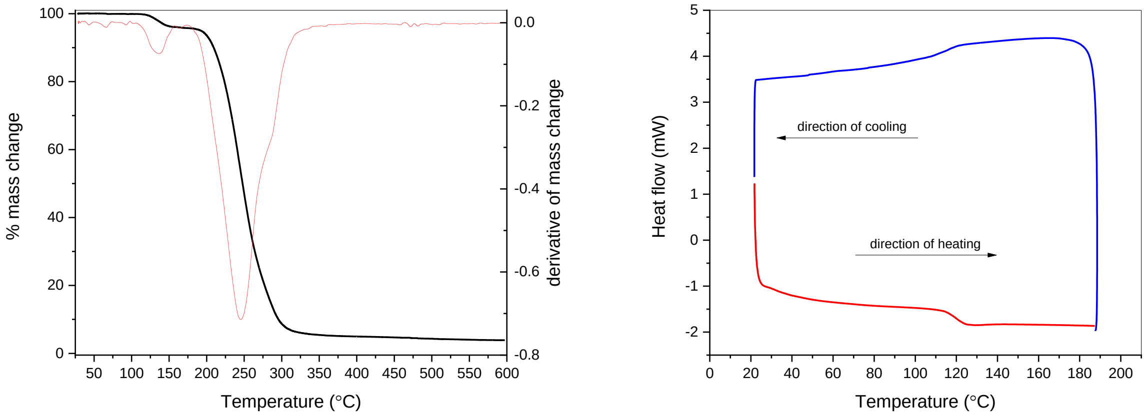


Fig. S12. (left) TGA (black = % mass loss, red = derivative of % mass loss) and (right) DSC (first cooling and first heating cycles) traces of 57% alternating trithio/thionocarbonate poly(**CS$_2$**-*co*-**1**) (Table 3, entry 6, $M_{n,SEC}$ = 8400 g mol^{-1}, $Đ_M$ =1.67; T_g = 120 °C; $T_{d,onset}$ = 178 °C; T_{d5} = 209 °C; $T_{d,max}$= 242 °C with 20% char remaining at 600 °C) measured under argon.

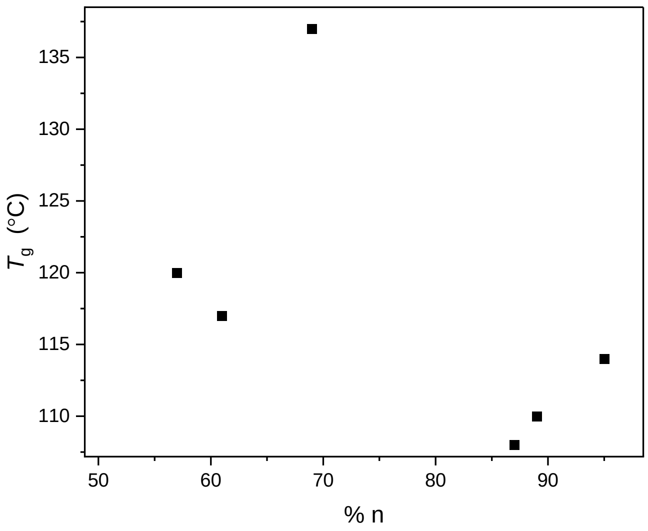


Fig. S13. % alternating trithio/thionocarbonate linkages (n in n:m:l ratio) *vs* T_g for poly(**CS_2**-*co*-**1**).

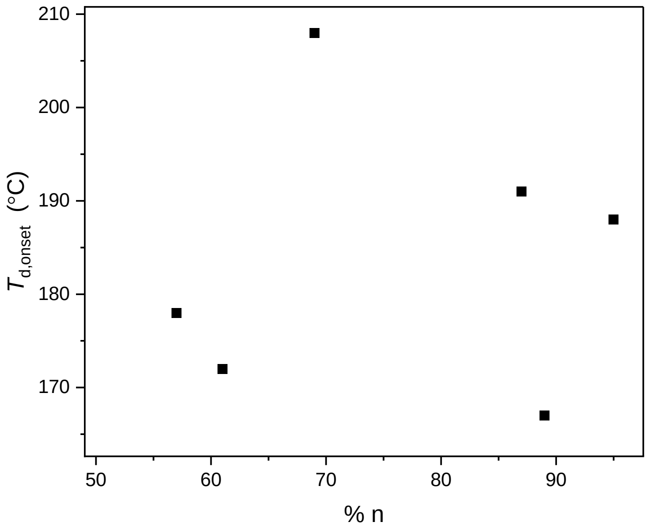


Fig. S14. % alternating trithio/thionocarbonate linkages (n in n:m:l ratio) *vs* $T_{d,onset}$ for poly(**CS_2**-*co*-**1**).

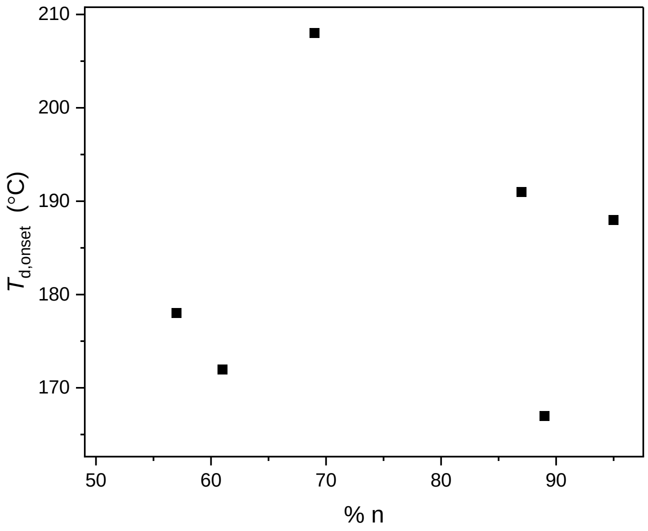


Fig. S15. %alternating trithio/thionocarbonate linkages (n in n:m:l ratio) *vs* T_{d5} for poly(**CS_2**-*co*-**1**).

5 WAXS profile of poly(CS_2-*co*-1)

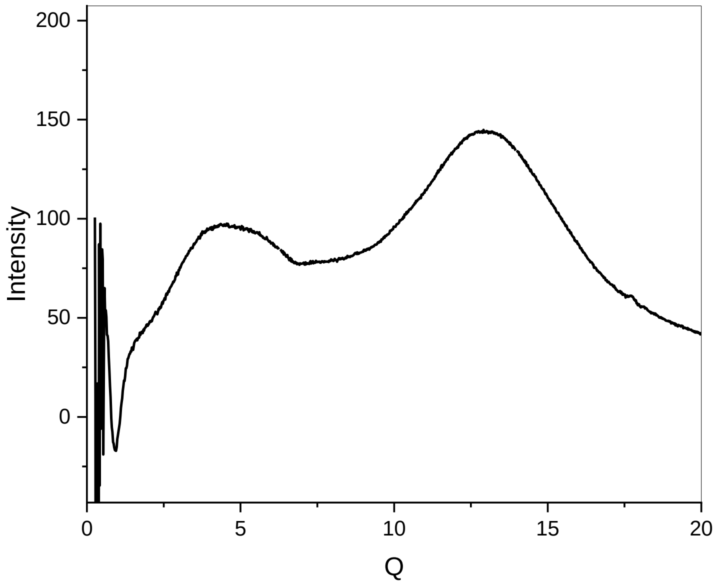


Fig. S16. WAXS profile of poly(**CS_2**-*co*-**1**) ($M_{n,SEC}$ = 14000 g mol^{-1}, $Đ_M$ =1.78, Table 1, entry 8).

6 SEC traces

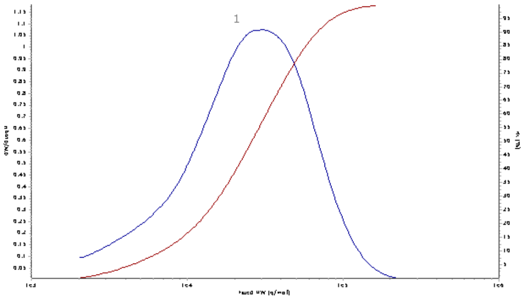


Fig. S17. Representative SEC trace of poly(**CS_2**-*co*-**1**) ($M_{n,SEC}$ = 15400 g mol^{-1}, $Đ_M$ = 2.13, Table 1, entry 3) formed through **CrSalen**-catalysed **1**/**CS_2** ROCOP.

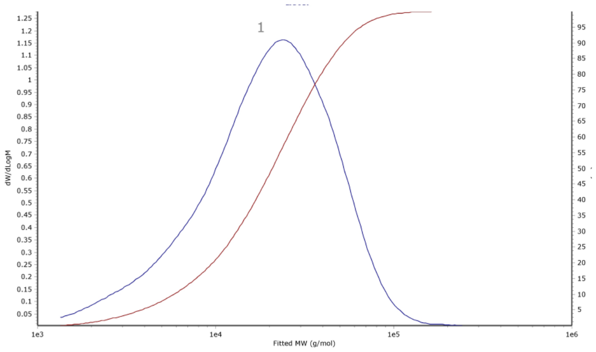


Fig. S18. SEC trace for poly(**2**) ($M_{n,SEC}$ = 12700 g mol^{-1}, $Đ_M$ = 2.05, Table 2, entry 2) formed through **CrSalen**-catalysed ROP of **2**.

7 Conversion of 1 *vs* $M_{n,SEC}$ plot

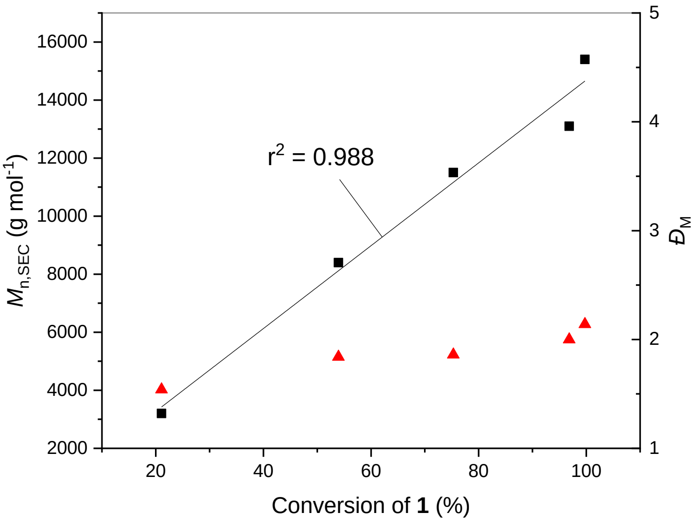


Fig. S19. Conversion of **1** *vs* $M_{n,SEC}$ (black, squares) and $Đ_M$ (red, triangles). Reaction performed in σ-dichlorobenzene at 80 °C with [**1**]$_0$:[CS_2]$_0$:[**CrSalen**]$_0$:[PPNCl]$_0$ loadings of 200:400:1:1. [**1**]$_0$ = 1.34 mol L^{-1}.

8 Polymer degradation experiments

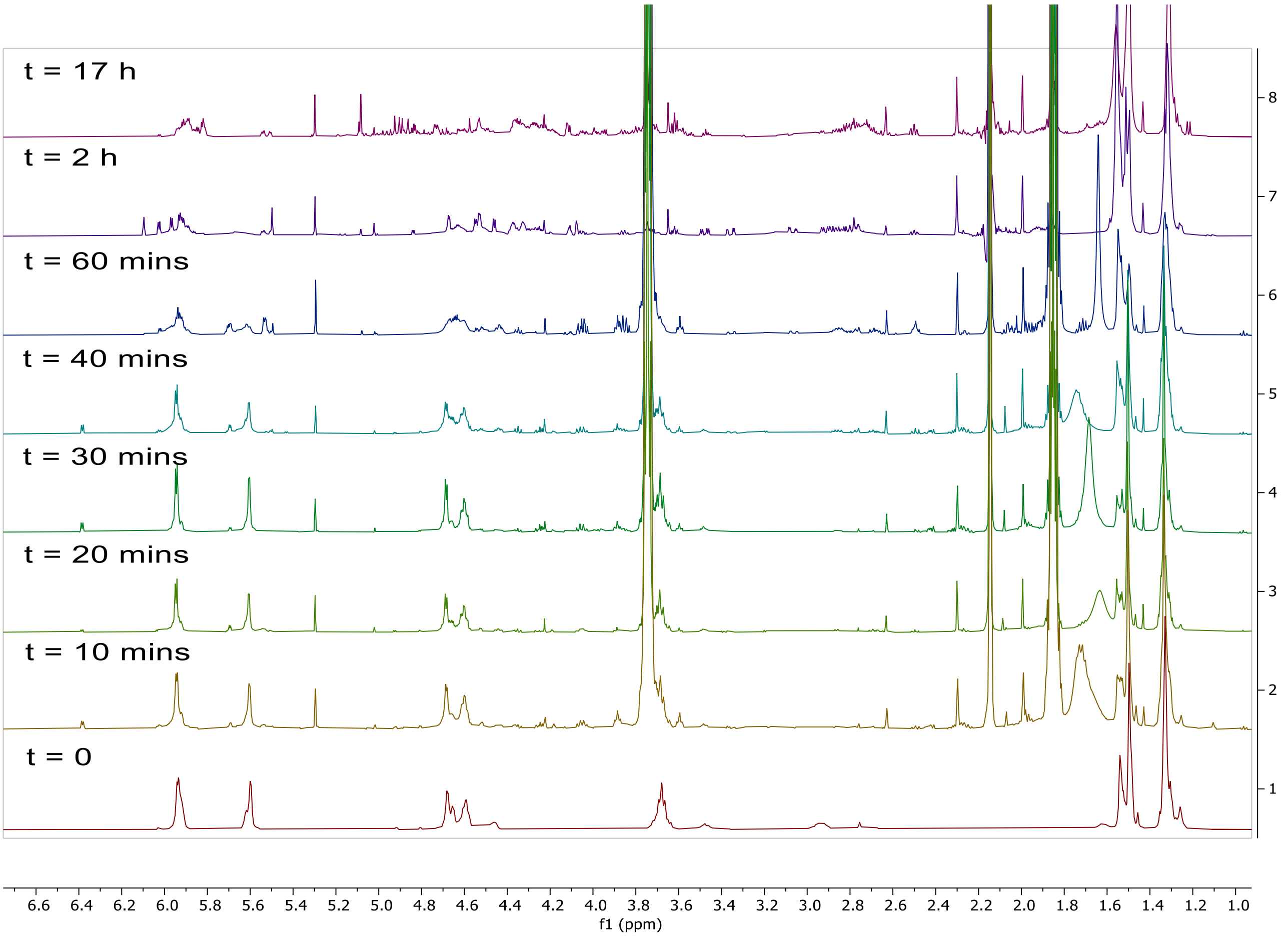
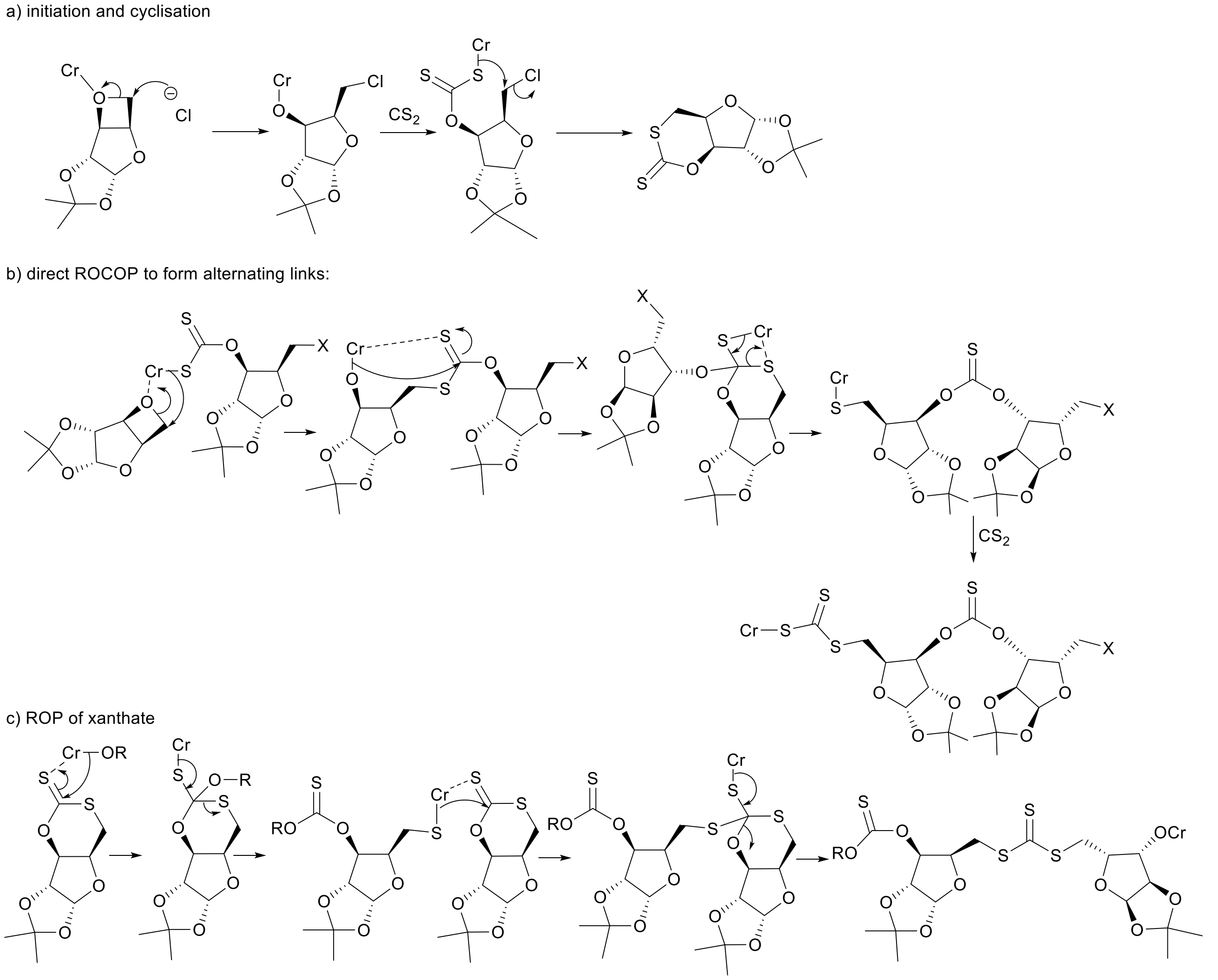
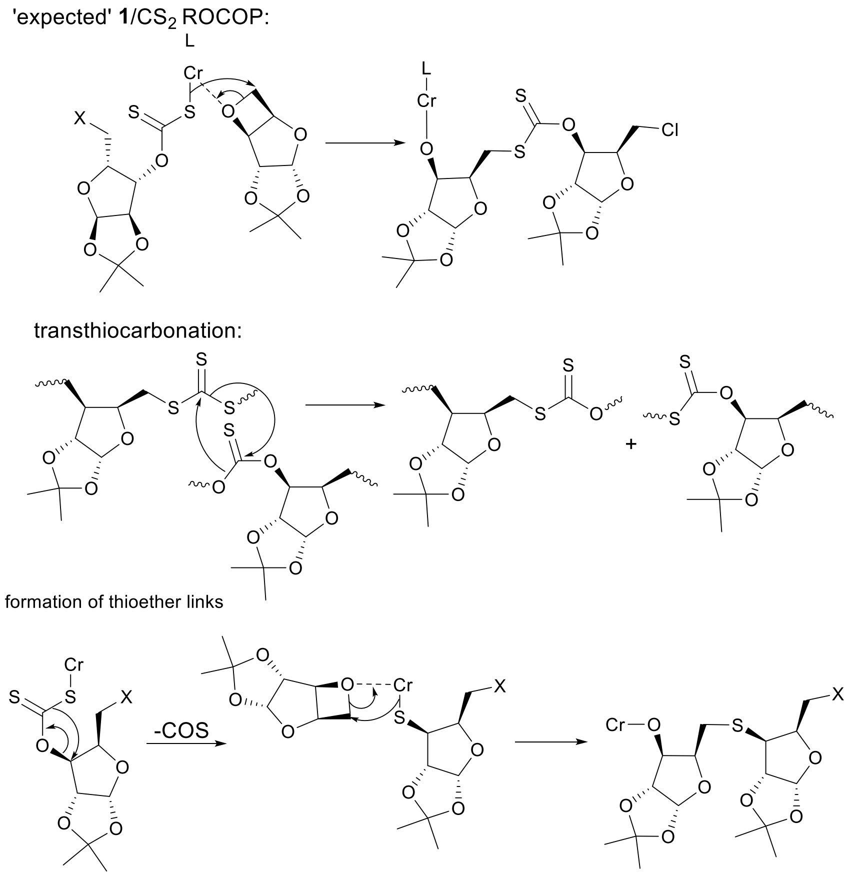


Fig. S20. ^{1}H NMR aliquots (CDCl$_3$) of a THF solution of poly(**CS$_2$**-*co*-**1**) ($M_{n,SEC}$ =8400 g mol^{-1}, $Đ_M$ = 1.67) following UV light (λ = 365 nm) in the presence of TTMSS (7.5 monomer equiv.)**.** The reaction was performed at 22 °C with [poly(**CS$_2$**-*co*-**1**)]$_0$ = 0.0267 mol L^{-1}.

9 Mechanistic considerations



Scheme S1. Possible mechanisms, yielding the observed products and polymer linkages, for a) the cycloaddition of **1** and CS$_2$ into **2**; b) the ROCOP of **1** and CS$_2$; c) the ROP of **2**.



Scheme S2. Possible mechanisms for the formation of xanthate and thioether linkages in poly(**CS₂**-co-**1**).

10 FTIR spectra of poly(CS_2-*co*-1)

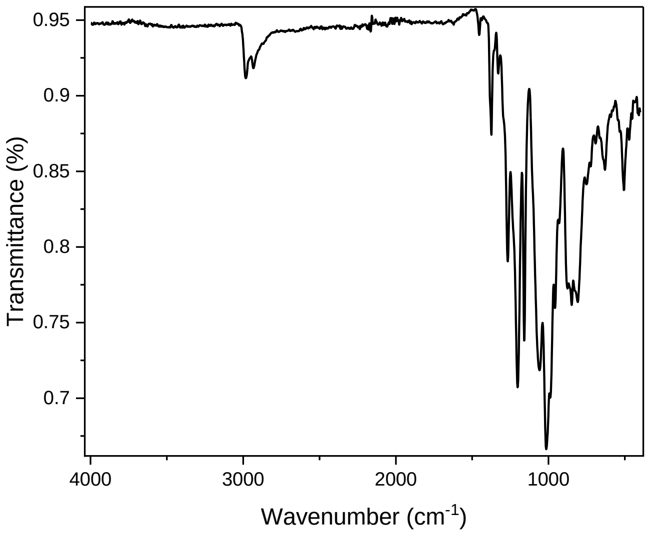


Fig. S21. FTIR spectrum of 89% alternating trithio/thionocarbonate poly(CS_2-*co*-1) ($M_{n,SEC}$ = 15400, $Đ_M$ = 2.14).

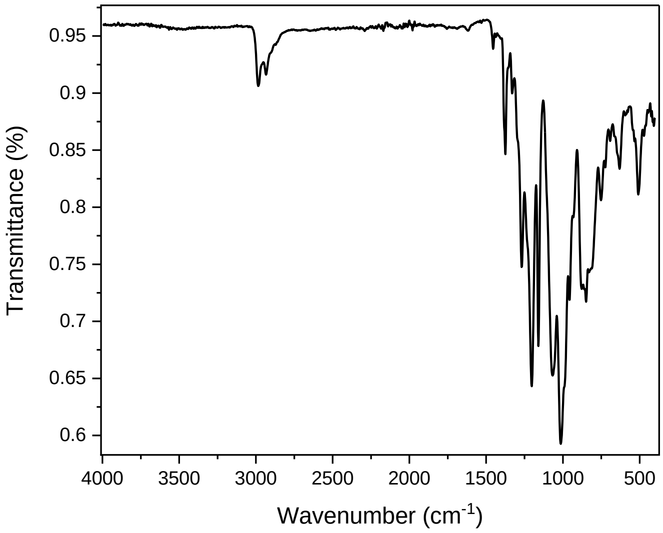


Fig. S22. FTIR spectrum of 57% alternating trithio/thionocarbonate poly(CS_2-*co*-1) ($M_{n,SEC}$ = 8400, $Đ_M$ = 1.67).

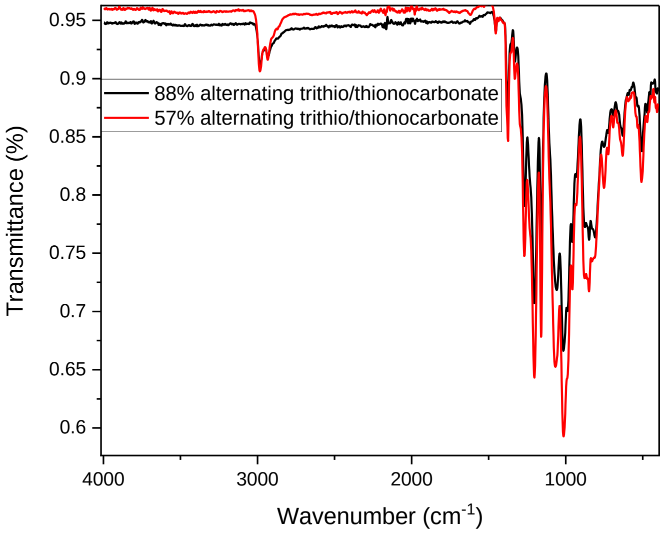


Fig. S23. Overlay of FTIR spectra of 88%(black) and 57% (red) alternating trithio/thionocarbonate poly(CS_2-*co*-1).

11 End-group titration by ^{31}P NMR spectroscopy

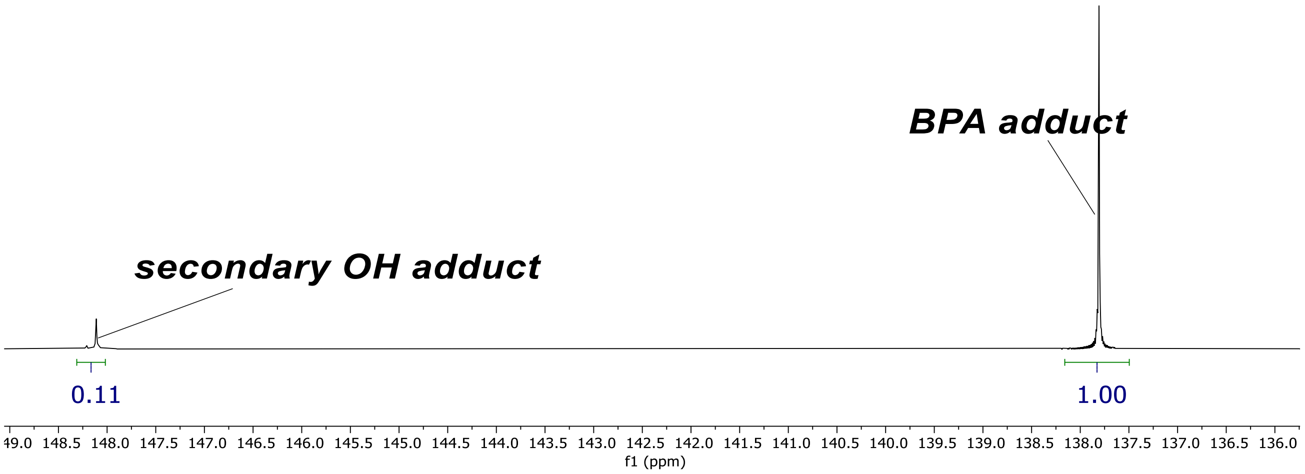


Fig. S24. ^{31}P{^{1}H} NMR spectrum of ($CDCl_3$) following the reaction of poly(**CS_2**-*co*-**1**) with 2-chloro-4,4,5,5-tetramethyl dioxaphospholane with bisphenol A used as an internal standard. The spectrum was collected with a long delay (T1 = 10 seconds) to ensure the data was quantitative.

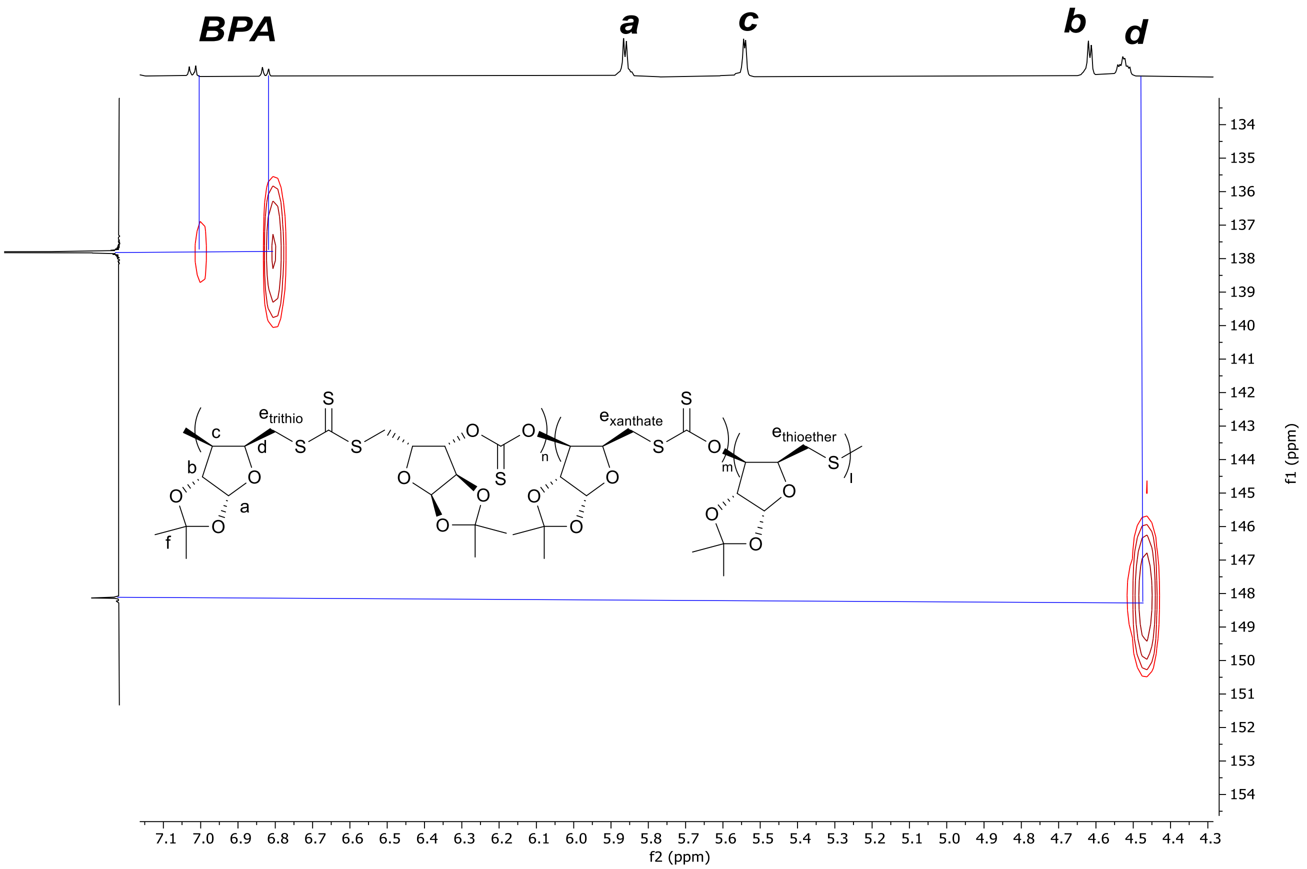


Fig. S25. ^{1}H-^{31}P{^{1}H} HMBC NMR spectrum ($CDCl_3$) following the reaction of poly(**CS_2**-*co*-**1**) with 2-chloro-4,4,5,5-tetramethyl dioxaphospholane with bisphenol A used as an internal standard.

12 References

1. T. M. McGuire, J. Bowles, E. Deane, E. H. E. Farrar, M. N. Grayson and A. Buchard, *Angew. Chem. Int. Ed.*, 2021, **60**, 4524-4528.
2. T. M. McGuire, E. F. Clark and A. Buchard, *Macromolecules*, 2021, **54**, 5094-5105.
3. E. M. López-Vidal, G. L. Gregory, G. Kociok-Köhn and A. Buchard, *Polym. Chem.*, 2018, **9**, 1577-1582.
4. A. Spyros, D. S. Argyropoulos and R. H. Marchessault, *Macromolecules*, 1997, **30**, 327-329.