Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

Synthesis and depolymerization of self-immolative poly(disulfide)s with saturated aliphatic backbones

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Materials

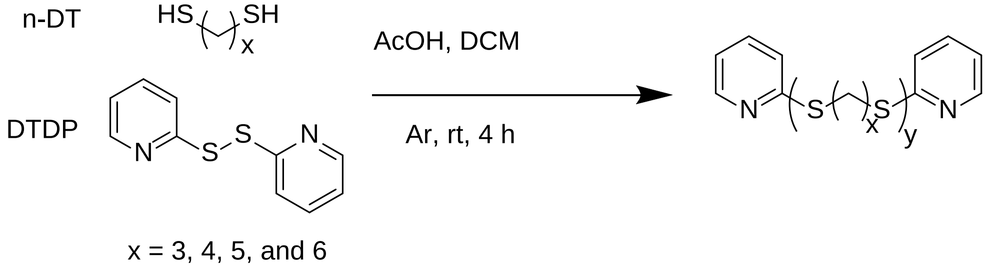
All synthetic procedures were carried out under ambient conditions unless otherwise stated. Most solvents and chemicals were purchased from Sigma Aldrich and used without further purification. Dithiothreitol (DTT) was purchased from Fischer Scientific.

Instruments

NMR spectra were recorded using a Bruker 400 MHz spectrometer with $CDCl_3$ as internal reference. For kinetic studies of depolymerization, ^1H NMR spectra were recorded using a Varian 400 MHz spectrometer with $CDCl_3$ as internal reference Size exclusion chromatography was performed using a system comprising a LC-20AD Shimadzu HPLC pump, a Shimadzu RID-10A refractive index detector, and a DAWN HELEOS 8 light scattering detector from Wyatt. The detector was a SPD-M20A PDA, equipped with a ResiPore column (7.5 × 300 mm) using 3 µm particles to provide an effective molecular weight range of 0–500’000 Da. Tetrahydrofuran (THF) was employed as solvent. Experiments were performed at 40 ^{o}C with flow rate of 1.0 mL min^{-1}. For molar weight calculations, samples were analyzed using a PMMA standard curve. Differential scanning calorimetry (DSC) analysis was performed with a PerkinElmer DSC 8000 using a scan rate of 40 ^{o}C min^{-1} from –20 to 100 ^{o}C under N_2 atmosphere.

Experimental procedures

Synthesis of polydisulfides



Synthesis of p3-DT

The procedure was adapted from previously published protocols.[S1] DTDP (483, 461, or 450 mg; 2.19, 2.09, or 2.04 mmol; 1.10, 1.05, or 1.025 equiv.) was added to a flame dried test tube equipped with a septum and magnetic stirrer and degassed for 10 min with Ar. Dry degassed dichloromethane, DCM (0.8 mL), was added to the solution which was stirred until becoming homogenous. 1,3-Propanedithiol (200 µL; 1.99 mmol; 1.0 equiv.) was added dropwise over 1 h, followed by addition of AcOH (23 µl; 0.40 mmol; 0.2 equiv.). The solution was allowed to react for 4 h at rt during which an insoluble rubbery solid was formed. Unfortunately, none of the desired compound could be detected.

Synthesis of p4-DT

The procedure was adapted from previously published protocols.[S1] DTDP (413, 394, or 385 mg; 1.88, 1.79, or 1.75 mmol; 1.1, 1.05, or 1.025 equiv.) was added to a flame dried test tube equipped with a septum and magnetic stirrer and degassed for 10 min with Ar. Dry degassed DCM (0.8 mL) was added to the solution which was stirred until becoming homogenous. 1,4-Butanedithiol (200 µL; 1.70 mmol; 1.0 equiv.) was added dropwise over 1 h, followed by addition of AcOH (20 µL; 0.34 mmol; 0.2 equiv.). The solution was allowed to react for 4 h at rt during which it became cloudy. The mixture was dissolved in $CHCl_3$, precipitated twice in excess MeOH and once in excess acetone, and stored at –18 °C for 1 h between each precipitation. The liquid was removed by decantation and the resulting solid was washed with acetone and pentane, and dried *in vacuo* overnight. The desired polymer came out as a white/slightly yellow solid with fair to good yields (see Table 1). **p4-DT$_{10}$**: ^{1}H NMR (400 MHz, $CDCl_3$) δ/ppm 8.49–8.45 (m, 2H), 7.75–7.60 (m, 4H), 7.127.06 (m, 2H), 2.71 (bs, 76H), 1.80 (bs, 76H). **p4-DT$_{20}$**: ^{1}H NMR (400 MHz, $CDCl_3$) δ/ppm 8.49-8.45 (m, 2H), 7.75–7.50 (m, 4H), 7.12–7.06 (m, 2H), 2.71 (bs, 101H), 1.80 (bs, 101H). **p4-DT$_{40}$**: ^{1}H NMR (400 MHz, $CDCl_3$) δ/ppm 8.49–8.45 (m, 2H), 7.75–7.50 (m, 4H), 7.12–7.06 (m, 2H), 2.71 (bs, 186H), 1.80 (bs, 186H).

Synthesis of p5-DT

The procedure was adapted from previously published protocols.[S1] DTDP (361, 345, or 337 mg; 1.64, 1.57, or 1.53 mmol; 1.1, 1.05, or 1.025 equiv.) was added to a flame dried test tube equipped with a septum and magnetic stirrer and degassed for 10 min with Ar. Dry degassed DCM (0.6 mL) was added to the solution which was stirred until becoming homogenous.

1,5-Pentanedithiol (200 µL; 1.49 mmol; 1.0 equiv.) was added dropwise over 1 h, followed by addition of AcOH (17 µL; 0.30 mmol; 0.2 equiv.). The solution was allowed to react for 4 h at rt during which it became cloudy. The mixture was dissolved in $CHCl_3$, precipitated twice in excess MeOH and once in excess acetone, and stored at –18 °C for 1 h between each precipitation. The liquid was removed by decantation and the resulting solid was washed with acetone and pentane and dried *in vacuo* overnight. The desired polymer came out as a white/slightly yellow solid with fair to good yields (see Table 1). **p5-DT$_{10}$**: ^1H NMR (400 MHz, $CDCl_3$) δ/ppm 8.48–8.44 (m, 2H), 7.75–7.50 (m, 4H), 7.11–7.05 (m, 2H), 2.68(t, J = 7.2 Hz, 76 H), 1.71 (qv, J = 7.4 Hz, 72H), 1.50 (qv, J = 7.0 Hz, 36H). **p5-DT$_{20}$**: ^1H NMR (400 MHz, $CDCl_3$) δ/ppm 8.48–8.44 (m, 2H), 7.75–7.50 (m, 4H), 7.11–7.05 (m, 2H), 2.68 (t, J = 7.2 Hz, 90 H), 1.71 (qv, J = 7.4 Hz, 90 H), 1.50 (qv, J = 7.0 Hz, 45 H). **p5-DT$_{40}$**: ^1H NMR (400 MHz, $CDCl_3$) δ/ppm 8.48–8.44 (m, 2H), 7.75–7.50 (m, 4H), 7.11–7.05 (m, 2H), 2.68 (t, J = 7.2 Hz, 128 H), 1.71 (qv, J = 7.4 Hz, 128 H), 1.50 (qv, J = 7.0 Hz, 64 H).

Synthesis of p6-DT

The procedure was adapted from previously published protocols.[S1] DTDP (317, 302, or 295 mg; 1.44, 1.37, or 1.34 mmol; 1.1, 1.05, or 1.025 equiv.) was added to a flame dried test tube equipped with a septum and magnetic stirrer and degassed for 10 min with Ar. Dry degassed DCM (0.4 mL) was added to the solution which was stirred until becoming homogenous. 1,6-Hexanedithiol (200 µL; 1.31 mmol; 1.0 equiv.) was added dropwise over 1 h, followed by addition of AcOH (15 µL; 0.26 mol; 0.2 equiv.). The solution was allowed to react for 4 h at rt during which it became cloudy. The mixture was dissolved in $CHCl_3$, precipitated twice in excess MeOH and once in excess acetone, and stored at –18 °C for 1 h between each precipitation. The liquid was removed by decantation and the resulting solid was washed with acetone and pentane and dried *in vacuo* overnight. The desired polymer came out as a white/slightly yellow solid with fair to good yields (see Table 1). **p6-DT$_{10}$**: ^1H NMR (400 MHz, $CDCl_3$) δ/ppm 8.48–8.44 (m, 2H), 7.75–7.50 (m, 4H), 7.11–7.05 (m, 2H), 2.68 (t, J = 7.3 Hz, 72 H), 1.69 (bs, 72 H), 1.42 (bs, 72 H). **p6-DT$_{20}$**: ^1H NMR (400 MHz, $CDCl_3$) δ/ppm 8.48–8.44 (m, 2H), 7.75–7.50 (m, 4H), 7.11–7.05 (m, 2H), 2.68 (t, J = 7.3 Hz, 100 H), 1.69 (bs, 100 H), 1.42 (bs, 100 H). **p6-DT$_{40}$**: ^1H NMR (400 MHz, $CDCl_3$) δ/ppm 8.48-8.44 (m, 2H), 7.75–7.50 (m, 4H), 7.11–7.05 (m, 2H), 2.68 (t, J = 7.3 Hz, 176 H), 1.69 (bs, 176 H), 1.42 (bs, 176 H).

Depolymerization

Using Et_3N (4.0 equiv.) under ambient conditions

Depolymerization was conducted in NMR tubes using ~10 mg polymer sample. The polymer was dissolved in $CDCl_3$ (0.9 ml) under ambient conditions. A $CDCl_3$ solution (100 µl) containing DTT (38–88 mM; 1.1 equiv. w.r.t. end-caps) and Et_3N (0.14–0.32 M; 4.0 equiv. w.r.t. end-caps) was added to the NMR tube to achieve a total volume of 1 ml. The tube was sealed with a rubber cap, kept at rt, and degradation was monitored using ^1H NMR.

Using Et_3N (4.0 equiv.) in Ar atmosphere

Depolymerization was conducted in NMR tubes using ~10 mg polymer sample. The polymer was dissolved in $CDCl_3$ (0.9 ml) in Ar atmosphere. A $CDCl_3$ solution (100 µl) containing DTT (38–88 mM, 1.1 equiv. w.r.t. end-caps) and Et_3N (0.14–0.32 M, 4.0 equiv. w.r.t. end-caps) was added to the NMR tube to achieve a total volume of 1 ml. The tube was sealed with a rubber cap, and degradation was monitored using ^1H NMR.

Using Et_3N (1.0 equiv.) in Ar atmosphere

Depolymerization was conducted in NMR tubes using ~10 mg polymer sample. The polymer was dissolved in $CDCl_3$ (0.9 ml) in Ar atmosphere. A $CDCl_3$ solution (100 µl) containing DTT (63 mM; 1.0 equiv. w.r.t. end-caps) and Et_3N (63 mM; 1.0 equiv. w.r.t. end-caps) was added to the NMR tube to achieve a total volume of 1 ml. The tube was melted to form an ampule, and degradation was monitored using ^1H NMR.

Using DBU in Ar atmosphere

Depolymerization was conducted in NMR tubes using ~10 mg polymer sample. The polymer was dissolved in degassed $CDCl_3$ (0.9 ml) in Ar atmosphere. A solution (100 µl) containing DTT (69 mM; 1.1 equiv. w.r.t. end-caps) and DBU (31–500 mM; 0.5–8.0 equiv. w.r.t. end-caps) was added to the NMR tube to achieve a total volume of 1 ml. The tube was sealed either with a rubber cap or melted to form an ampule, and the degradation was monitored using ^1H NMR.

Using DBU in Ar atmosphere for product isolation

p4-DT_{20} (40 mg, 13 µmol, 1.0 equiv.) was added to a 8 ml vial and dissolved in degassed $CDCl_3$ (3.6 ml) in Ar atmosphere. A solution (400 µl) containing DTT (69 mM; 1.1 equiv. w.r.t. end-caps) and DBU (63 mM; 1.0 equiv. w.r.t. end-caps) was added to the vial to achieve a total volume of 4 ml and sealed with a screw cap. The solution was allowed to react for 24 h. Depolymerization products were isolated by preparative TLC using pentane:Et_2O (20/1 v/v) as eluent. 1,2-Dithiane: ^1H NMR (400 MHz, $CDCl_3$) δ/ppm 2.82 (bs, 4H), 1.95 (bs, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ/ppm 33.40, 27.84. Spectral values are in accordance with literature.[S2]

p5-DT_{20} (40 mg, 13 µmol, 1.0 equiv.) was added to a 8 ml vial and dissolved in degassed $CDCl_3$ (3.6 ml) in Ar atmosphere. A solution (400 µl) containing DTT (69 mM; 1.1 equiv. w.r.t. end-caps) and DBU (0.25 M; 4.0 equiv. w.r.t. end-caps) was added to the vial to achieve a total volume of 4 ml and sealed with a screw cap. The solution was allowed to react for 15 days. Depolymerization products were isolated by preparative TLC using pentane:Et_2O (20/1 v/v) as eluent. 1,2-Dithiepane: ^1H NMR (400 MHz, $CDCl_3$) δ/ppm 2.81 (t, J = 6.2 Hz, 4H), 2.01 (q, J = 6.1 Hz, 4H), 1.75 (q, J = 6.1 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ/ppm 39.51, 30.29, 26.28. Spectral values are in accordance with literature.[S2]

p6-DT_{20} (40 mg, 11 µmol, 1.0 equiv.) was added to a 8 ml vial and dissolved in degassed $CDCl_3$ (3.6 ml) in Ar atmosphere. A solution (400 µl) containing DTT (61 mM; 1.1 equiv. w.r.t. end-caps) and DBU (0.22 M; 4.0 equiv. w.r.t. end-caps) was added to the vial to achieve a total volume of 4 ml and sealed with a screw cap. The solution was allowed to react for 11 days (p6-DT_{20}). Depolymerization products were isolated by preparative TLC using pentane:Et_2O (20/1 v/v) as eluent. 1,2,9,10-Tetrathiacyclohexadecane: ^1H NMR (400 MHz, $CDCl_3$) δ/ppm 2.74 (t, J = 7.4 Hz, 4H), 1.78–1.70 (m, 8H), 1.53–1.47 (m, 8H). ^{13}C NMR (100 MHz, $CDCl_3$) δ/ppm 39.59, 28.77, 27.67. Spectral values are in accordance with literature.[S2]

DSC

Samples of ~10 mg polymers were crimped in aluminum pans (volume = 50 µL) and rapidly cooled down to –20 °C in N_2 atmosphere in the DSC apparatus. Thermal program: 1) Hold 0.2 min at –20 °C; 2) Heat –20 °C to 100 °C at 40 °C min^{-1}; 3) Hold 0.2 min at 100 °C; 4) Cool 100 °C to –20 °C at 40 °C min^{-1}; 5) Hold 0.2 min at –20 °C; 6) Heat –20 °C to 100 °C at 40 °C min^{-1}; 7) Cool 100 °C to –20 °C at 40 °C min^{-1}. Melting temperature (T_m) was determined as the maximum of the melting peak on the second heat scan.

Supporting figures

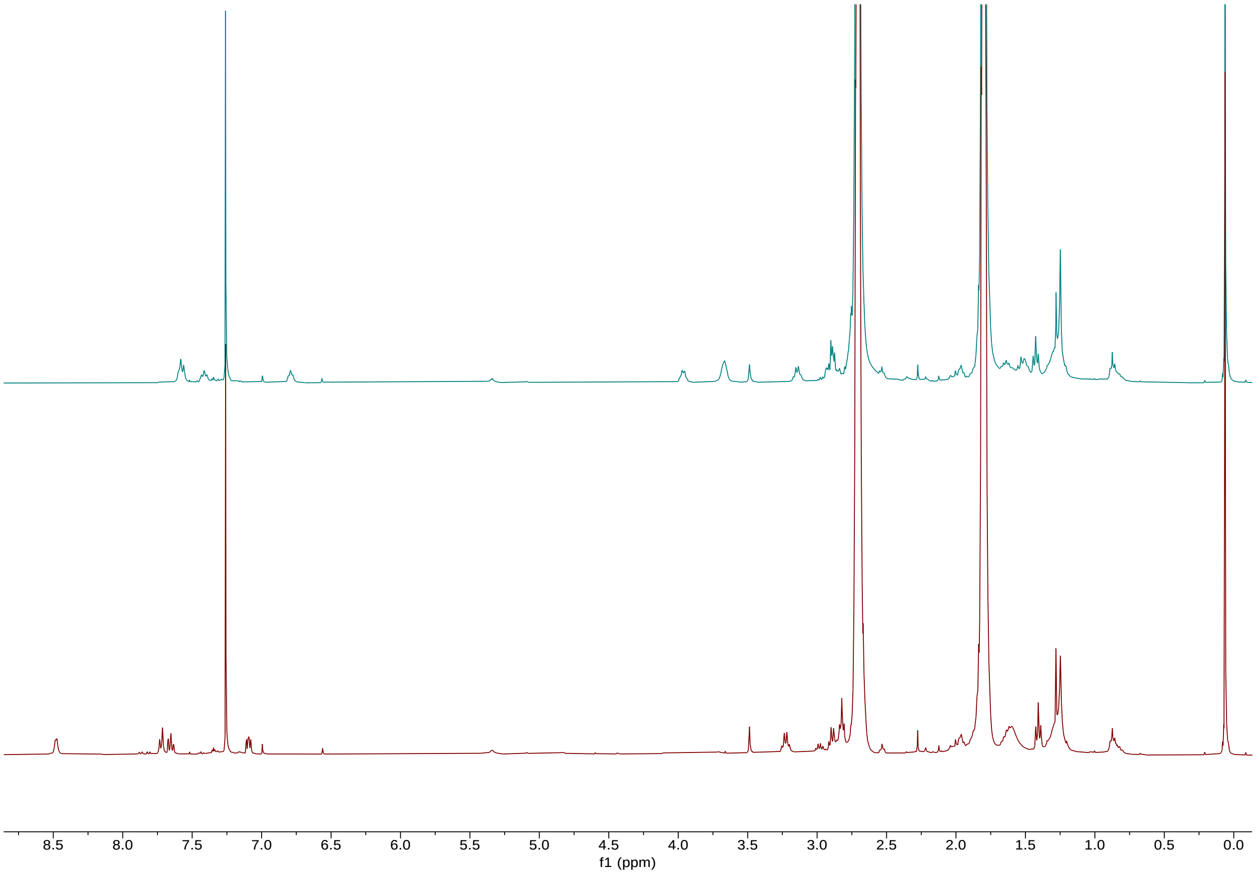


Fig. S1. ^{1}H NMR spectra of p4-DT (3.1 mM) before (bottom) and after (top) addition of DTT (6.9 mM; 1.1 equiv. w.r.t. end-caps) showing removal of thiopyridinic end-cap by DTT at rt in $CDCl_3$.

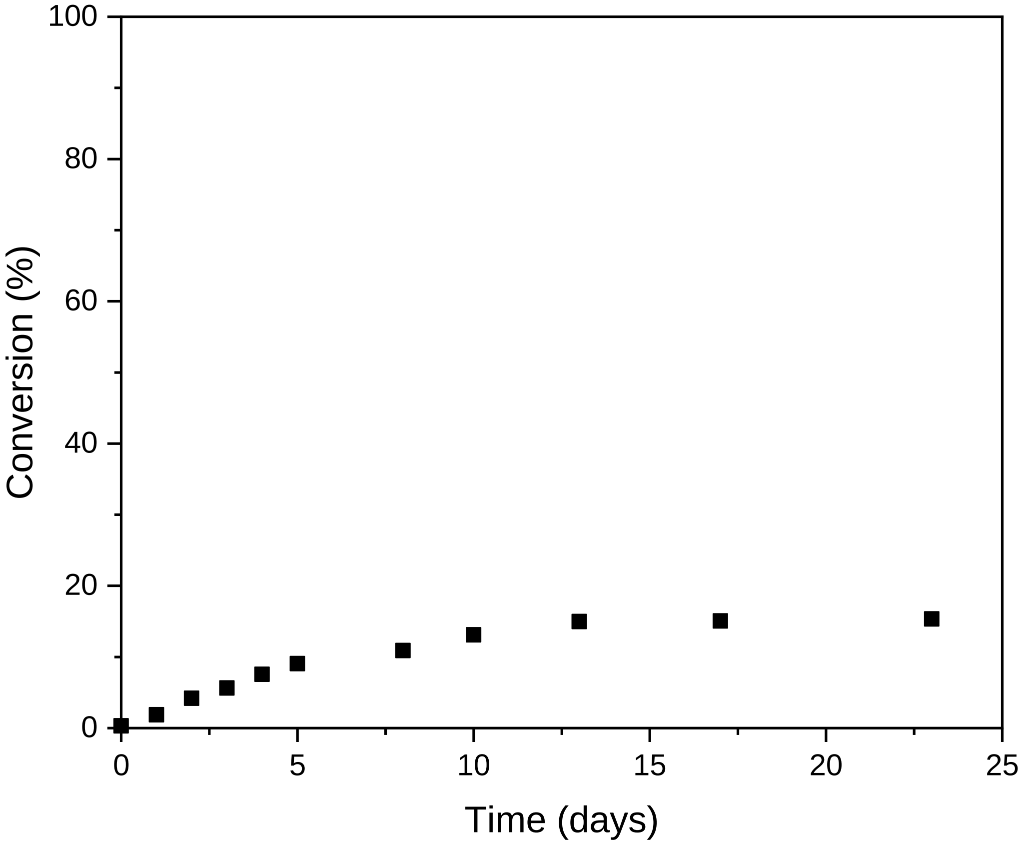


Fig. S2. Conversion of p4-DT$_{20}$ (3.1 mM) to c4-DT using DTT (6.9 mM; 1.1 equiv. w.r.t. end-caps) under ambient conditions measured by ^{1}H NMR at rt in CDCl$_3$.

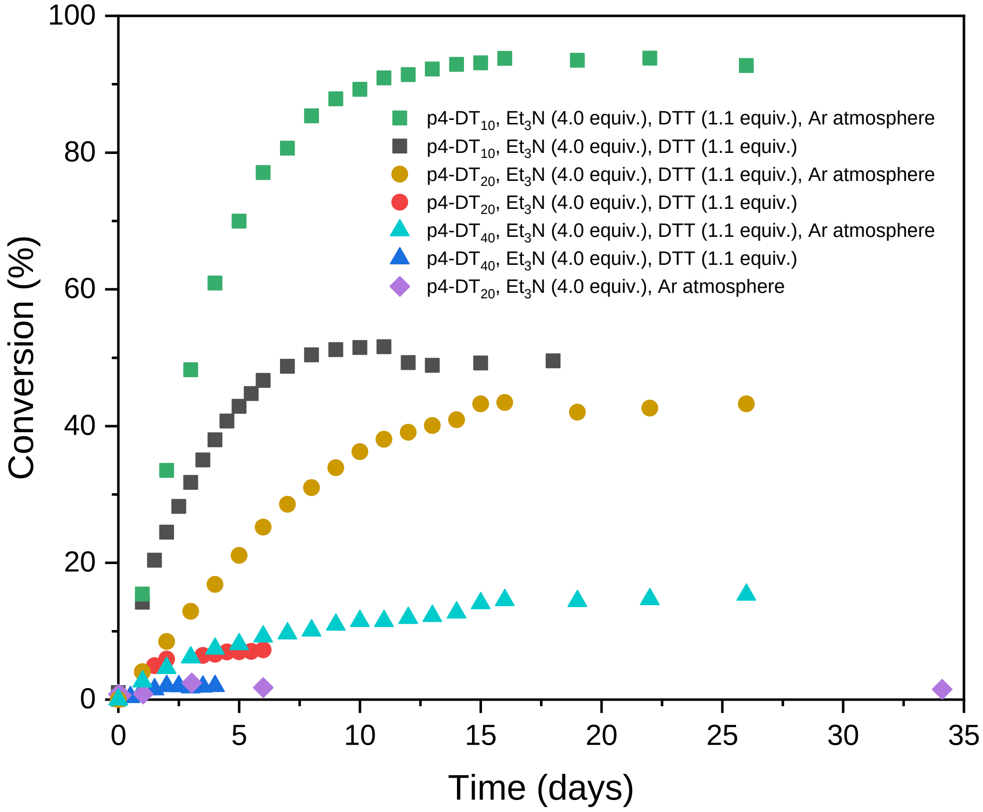


Fig. S3. Kinetic traces of conversion p4-DT(1.7–4.0 mM) to c4-DT using DTT (3.8–8.8 mM; 1.1 equiv. w.r.t. endcaps) and Et$_3$N (14–32 mM; 4 equiv. w.r.t end-caps) under ambient conditions or in Ar atmosphere measured by ^{1}H NMR at rt in CDCl$_3$.

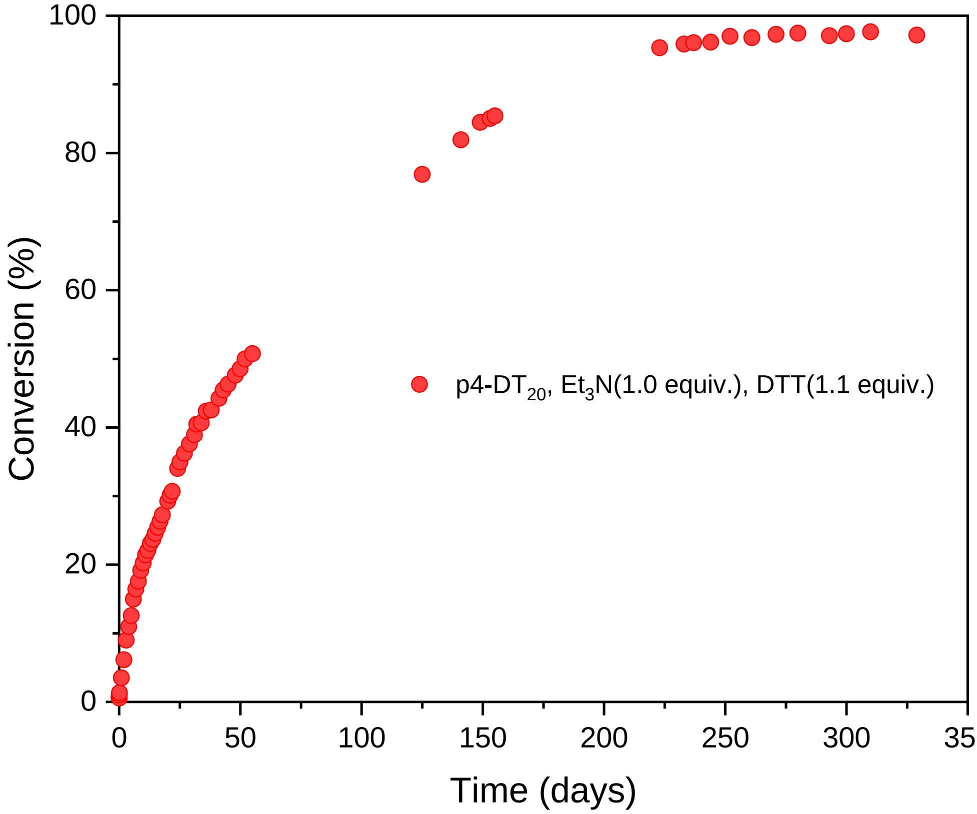


Fig. S4. Kinetic trace of conversion p4-DT (3.1 mM) to c4-DT using DTT (6.3 mM; 1.0 equiv. w.r.t. end-caps) and Et$_3$N (6.3 mM; 1.0 equiv. w.r.t. end-caps) in an ampule in Ar atmosphere measured by ^{1}H NMR at rt in CDCl$_3$.

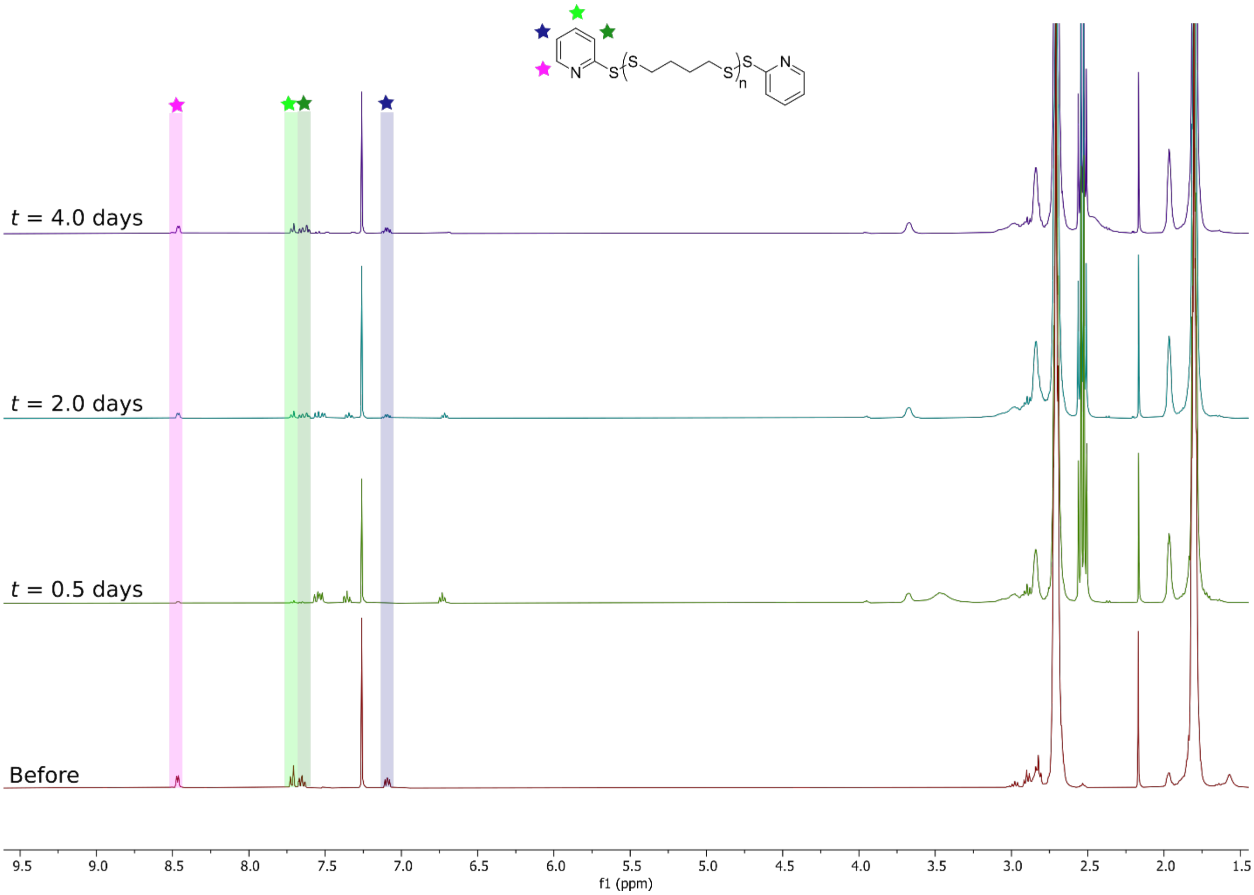


Fig. S5. ^{1}H NMR spectra showing reattachment of thiopyridinic end-cap during depolymerization of p4-DT$_{20}$ using DTT (6.9 mM; 1.1 equiv. w.r.t. end-caps) and Et$_3$N (25 mM; 4.0 equiv. w.r.t. end-caps) under ambient conditions at rt in CDCl$_3$.

Table S1. Initial rates estimated for formation of c4-DT from p4-DT.[a]

Sample	Atmosphere	Initial rate × 10^8 (s^{-1})
p4-DT_{10}	Ambient	13
p4-DT_{20}	Ambient	3.7
p4-DT_{40}	Ambient	1.3
p4-DT_{10}	Ar	14
p4-DT_{20}	Ar	3.7
p4-DT_{40}	Ar	2.4

[a] Initial rates were extracted from the kinetic traces in Fig. S4, i.e. using the rate of cx-DT formation observed in ^{1}H NMR during the first day of depolymerization.

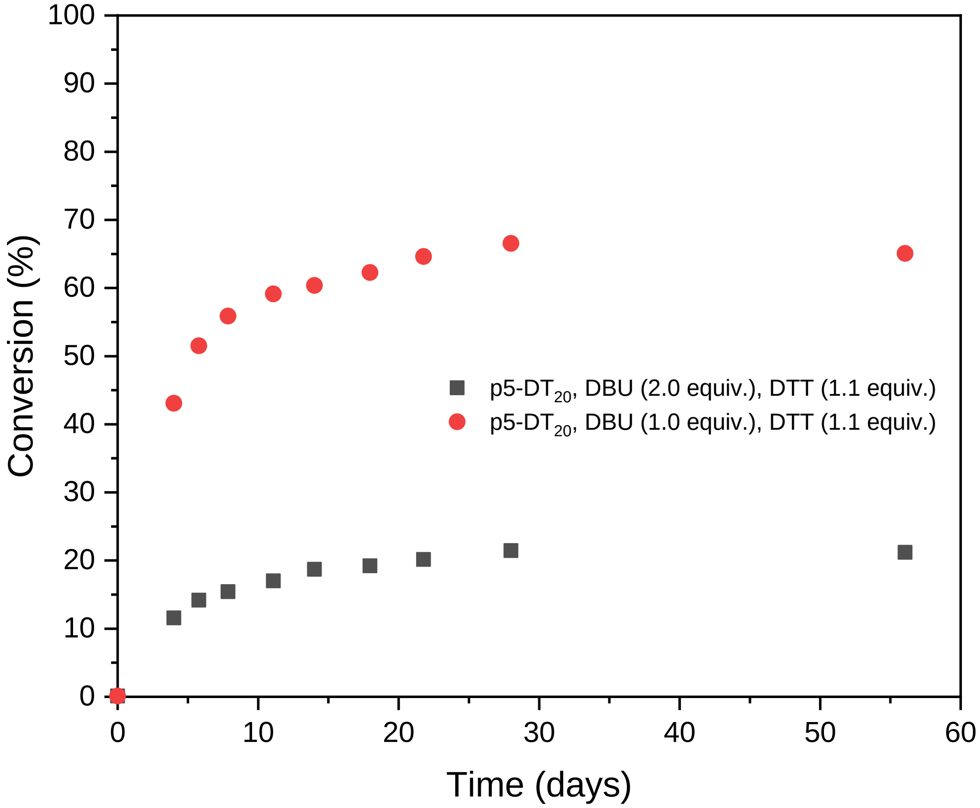


Fig. S6. Kinetic traces of conversion of p5-DT_{20} (3.1mM) to c5-DT in $CDCl_3$ using DTT (6.9 mM; 1.1 equiv. w.r.t. end-caps) and varying amounts of DBU (6.3–12.5 mM; 1–2.0 equiv. w.r.t. end-caps) in ampules under ambient conditions measured by ^1H NMR at rt in $CDCl_3$.

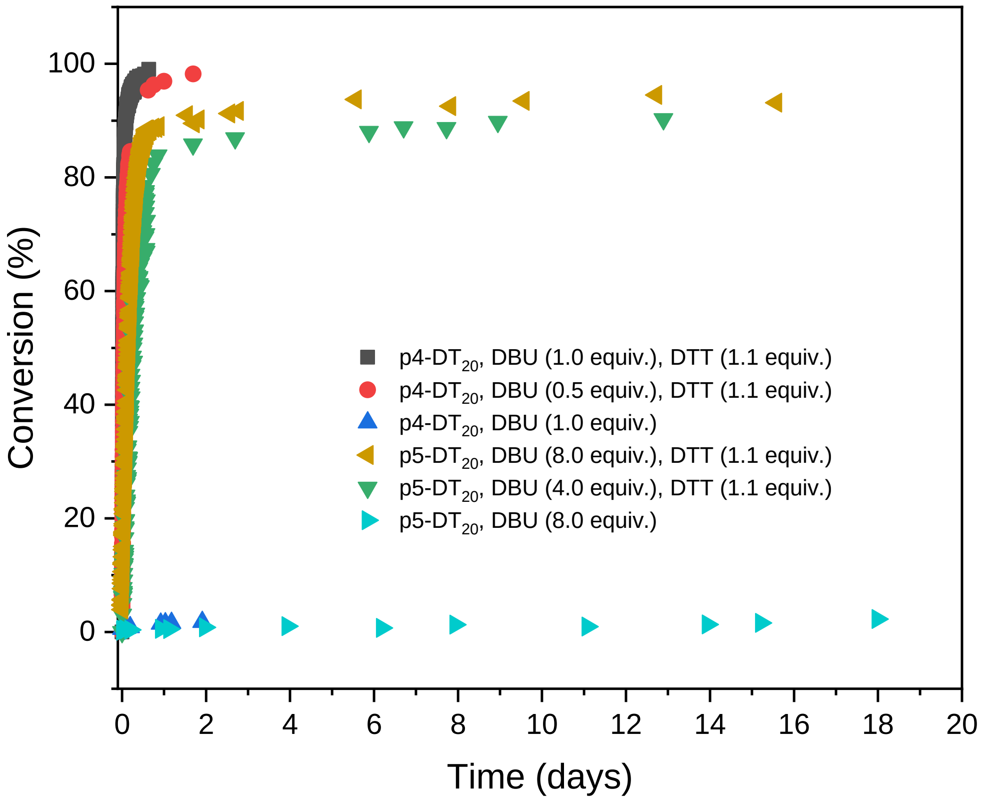


Fig. S7. Full graph of kinetic traces shown in Fig. 1b of conversion of p4-DT$_{20}$ (3.1 mM) and p5-DT$_{20}$ (3.1 mM) to c4-DT and c5-DT, respectively, in the presence of varying concentrations of DBU (3.1–50 mM; 0.5–8.0 equiv.) and in the presence or absence of DTT (used for end-cap removal) as measured from integrals at 1.80 and 1.95 ppm for p4-DT, and at 1.50 and 2.01 ppm for p5-DT in ^{1}H NMR. All experiments were conducted under Ar atmosphere at rt in CDCl$_3$ and, in the case of p5-DT, in ampules as well; equivalents are reported w.r.t. end-caps.

Fig. S8. TLC analysis using pentane:Et_2O (20:1 v/v) as eluent for the reaction of p6-DT_{20} (2.8 mM) with DTT (6.1 mM; 1.1 equiv. w.r.t. end-caps) and DBU (22 mM; 4.0 equiv. w.r.t. end-caps). Iodine dip was used to visualize spots. Top spot was isolated by preparative TLC (using the same eluent) and identified as 1,2,9,10-tetrathiacyclohexadecane on the basis of ^1H NMR and ^{13}C NMR.

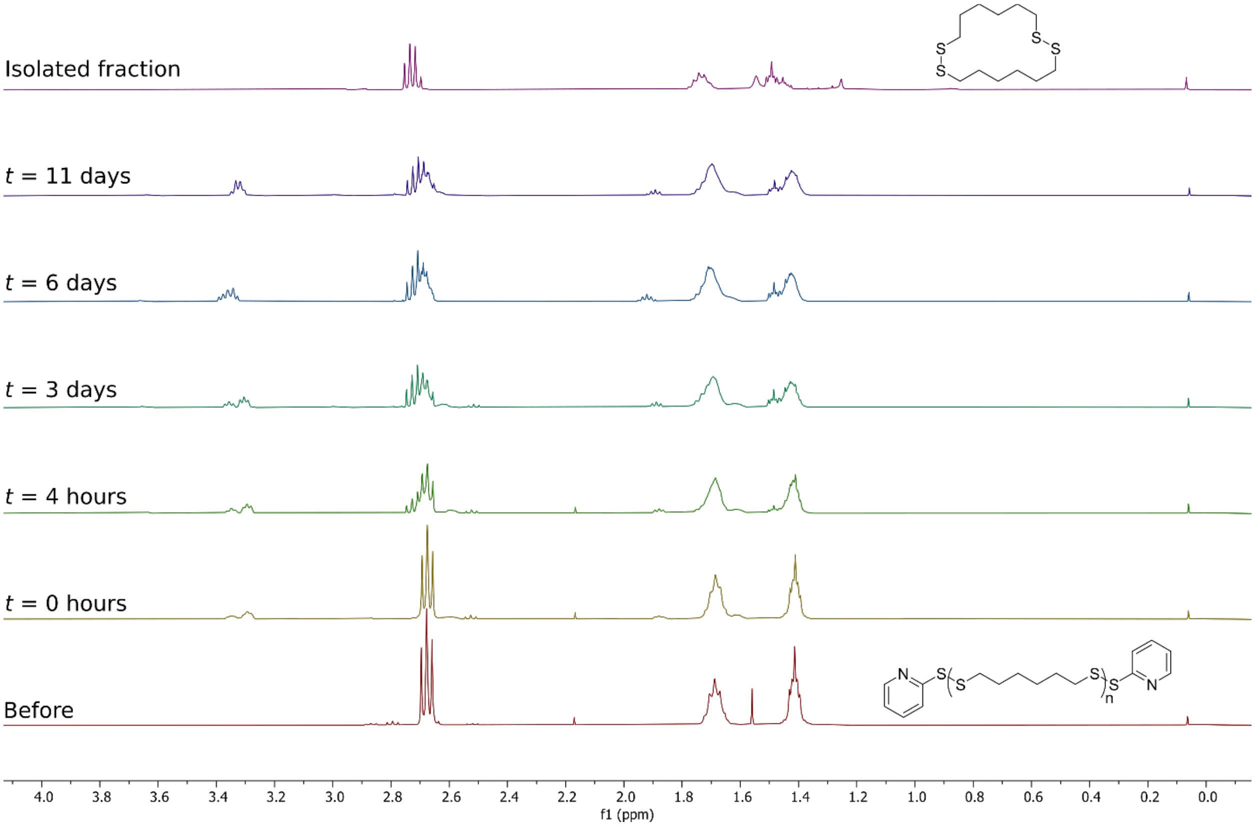


Fig. S9. ^{1}H NMR spectra of p6-DT$_{20}$ (2.8 mM) before and after being depolymerized using DTT (6.1 mM; 1.1 equiv. w.r.t. end-caps) and DBU (22 mM; 4.0 equiv. w.r.t. end-caps) at rt in $CDCl_3$, and the resulting isolated fraction identified as 1,2,9,10-tetrathiacyclohexadecane.

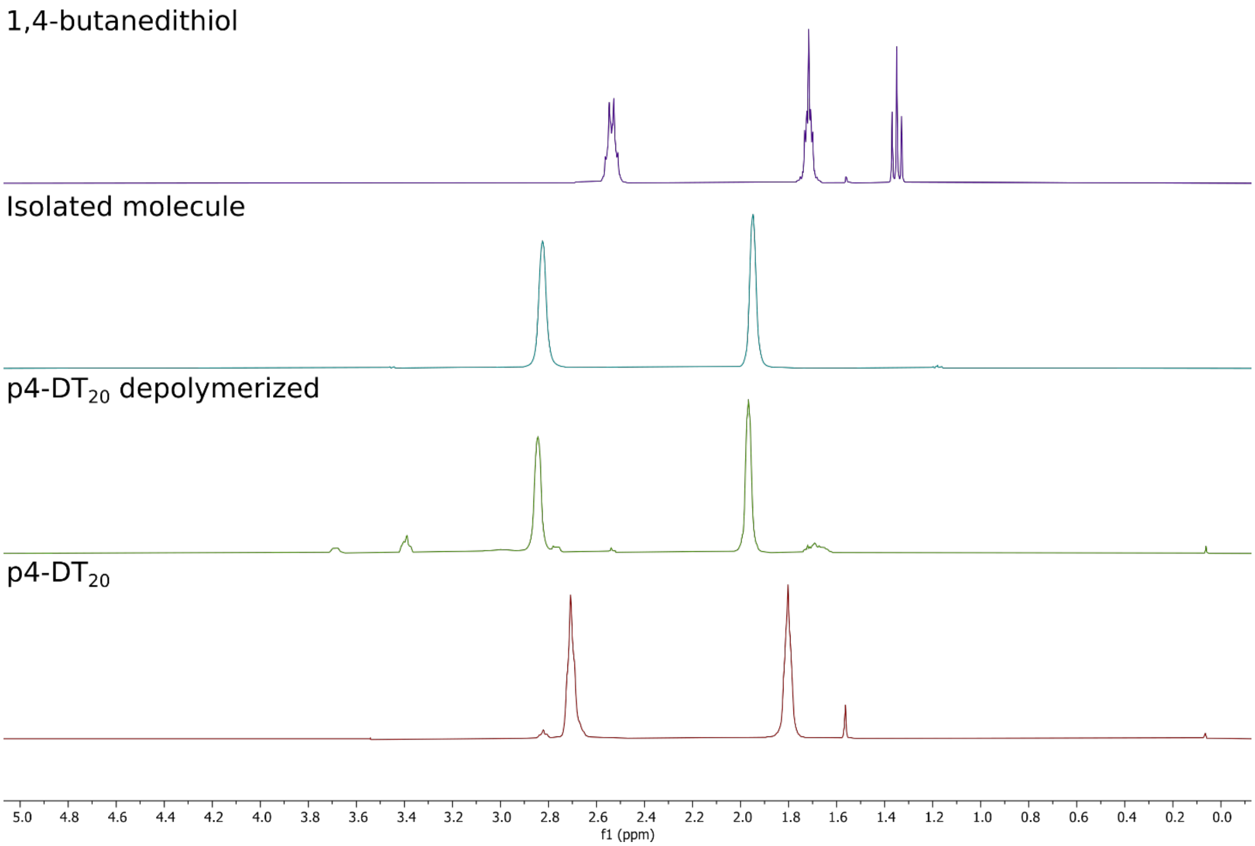


Fig. S10. ^{1}H NMR spectra of p4-DT$_{20}$, p4-DT$_{20}$ (3.1 mM) after being depolymerized using DTT (6.9 mM; 1.1 equiv. w.r.t. end-caps) and DBU (6.3 mM, 1.0 equiv. w.r.t. end-caps) at rt in CDCl$_3$, the isolated small molecule identified as 1,2-dithiane by spectral values, and 1,4-butanedithiol.

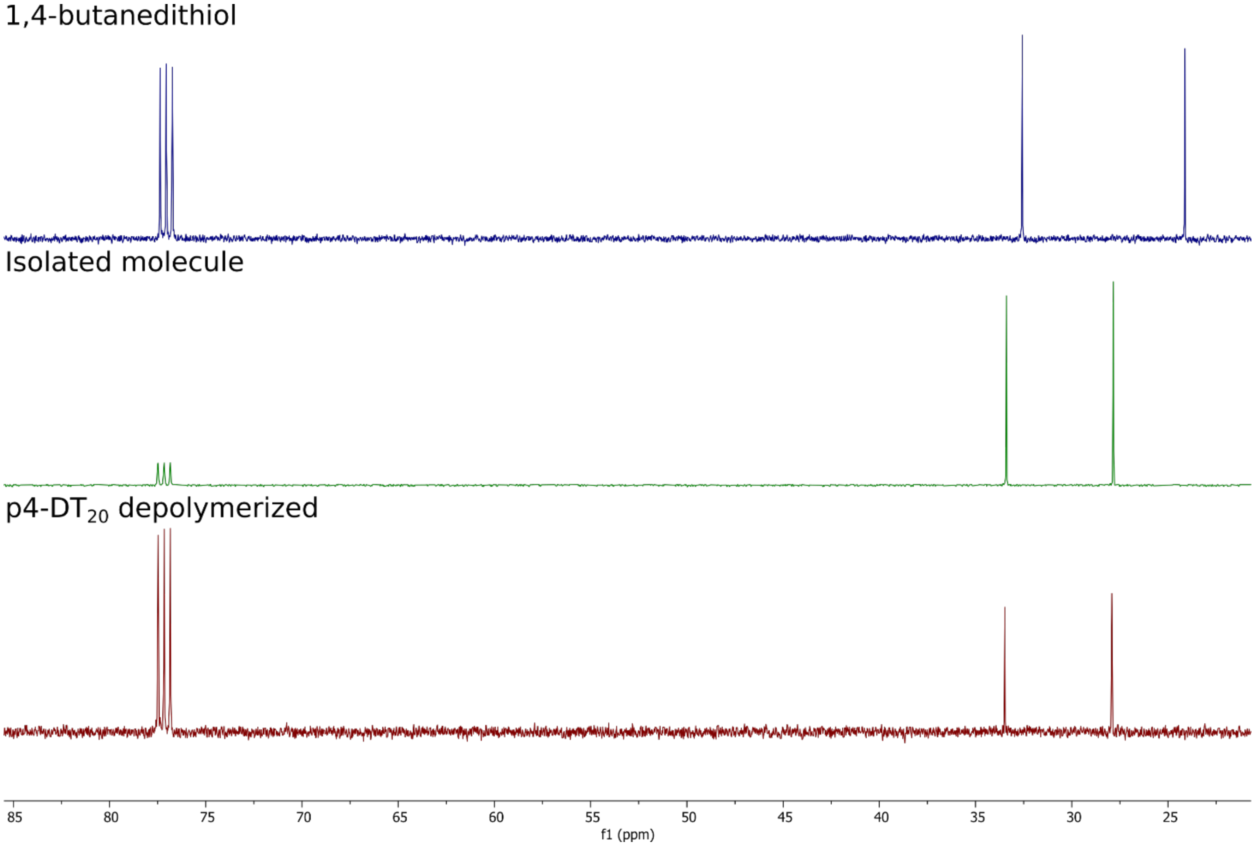


Fig. S11. ^{13}C NMR spectra of p4-DT$_{20}$ (3.1 mM) after being depolymerized using DTT (6.9 mM; 1.1 equiv. w.r.t. end-caps) and DBU (6.3 mM; 1.0 equiv. w.r.t. end-caps) at rt in CDCl$_3$, the isolated small molecule identified as 1,2-dithiane by spectral values, and 1,4-butanedithiol.

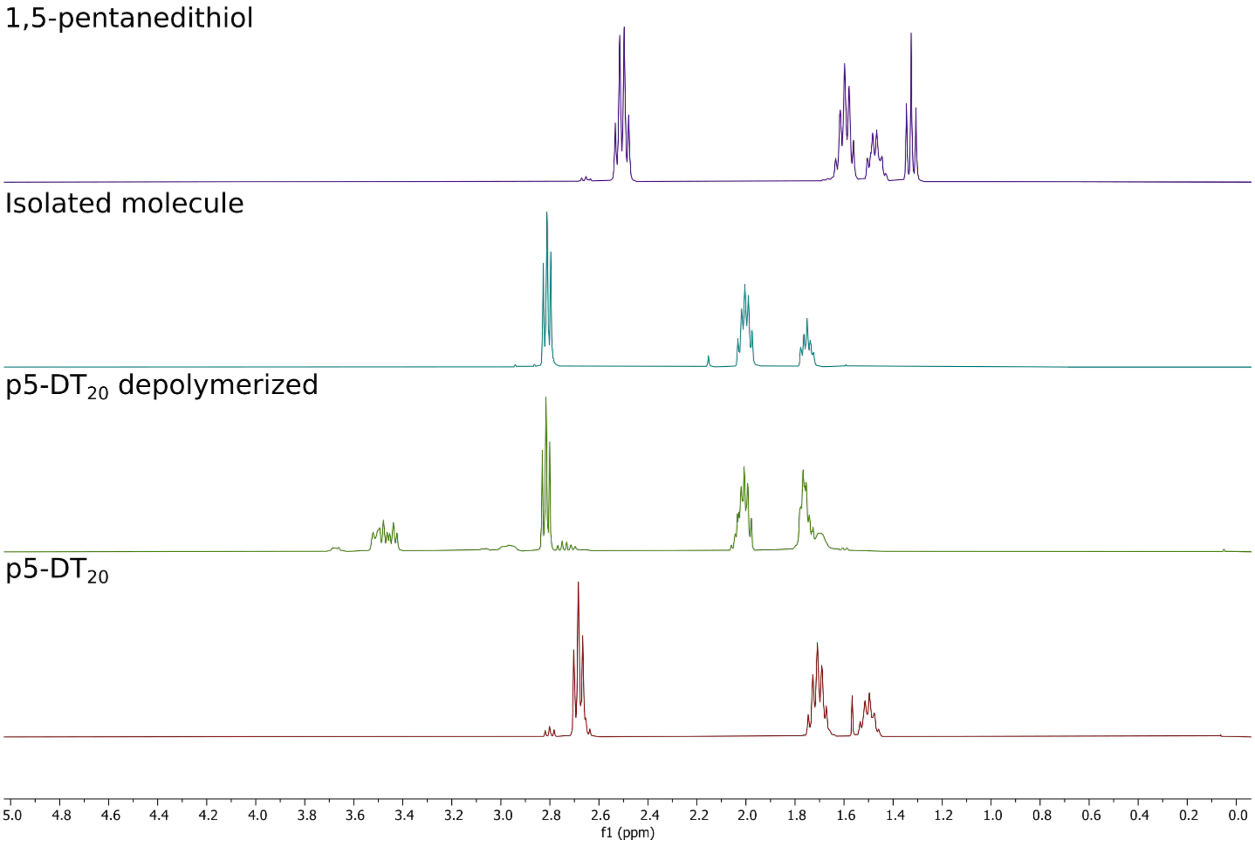


Fig. S12. ^{1}H NMR spectra of p5-DT$_{20}$, p5-DT$_{20}$ (3.1 mM) after being depolymerized using DTT (6.9 mM; 1.1 equiv. w.r.t. end-caps) and DBU (25 mM; 1.0 equiv. w.r.t. end-caps) at rt in CDCl$_3$, the isolated small molecule identified as 1,2-dithiepane by spectral values, and 1,5-pentanedithiol.

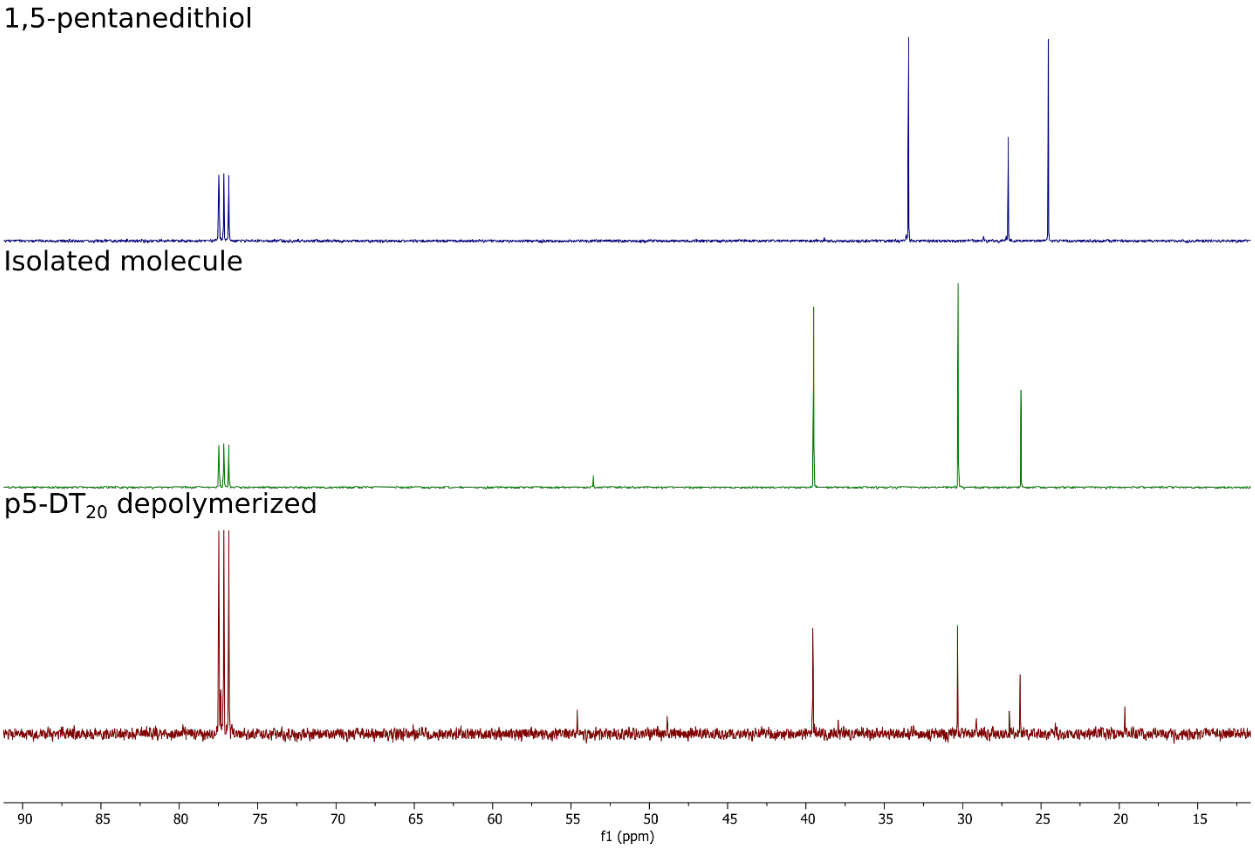


Fig. S13. ^{13}C NMR spectra of p5-DT$_{20}$ (3.1 mM) after being depolymerized using DTT (6.9 mM; 1.1 equiv. w.r.t. end-caps) and DBU (25 mM; 1.0 equiv. w.r.t. end-caps) at rt in CDCl$_3$, the isolated small molecule identified as 1,2-dithiepane by spectral values, and 1,5-pentanedithiol.

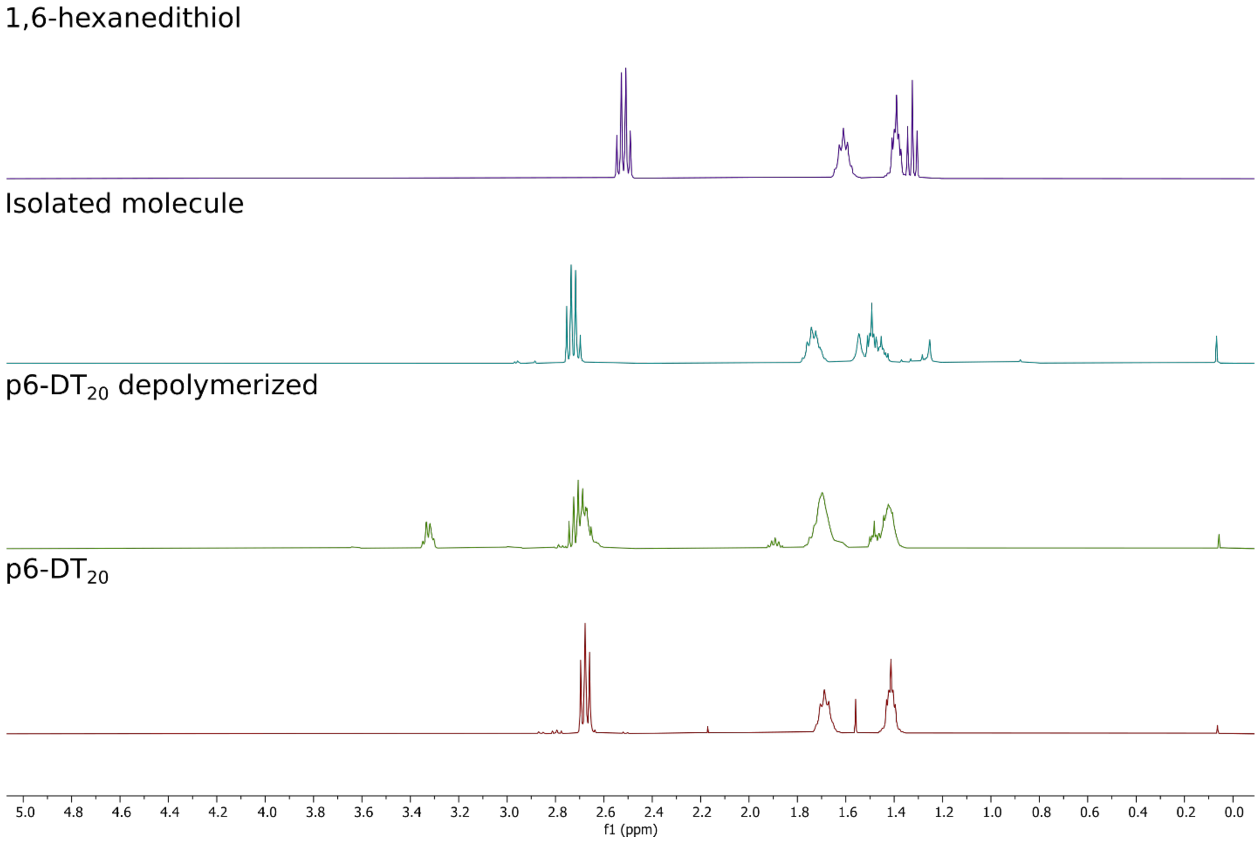


Fig. S14. ^{1}H NMR spectra of p6-DT$_{20}$, p6-DT$_{20}$ (2.8 mM) after being depolymerized using DTT (6.1 mM; 1.1 equiv. w.r.t. end-caps) and DBU (22 mM; 1.0 equiv. w.r.t. end-caps) at rt in $CDCl_3$, the isolated small molecule identified as 1,2,9,10-tetrathiacyclohexadecane by spectral values, and 1,6-hexanedithiol.

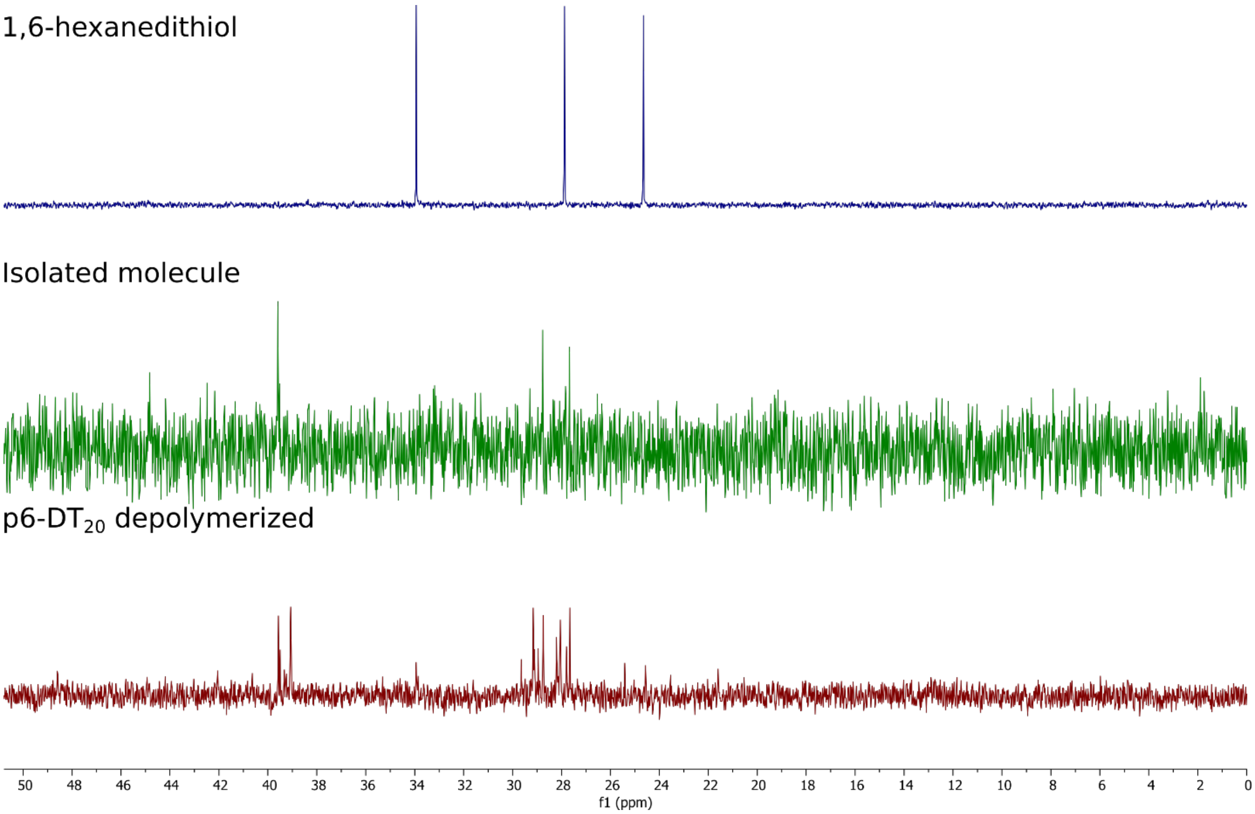


Fig. S15. ^{13}C NMR spectra of p6-DT$_{20}$ (2.8 mM) after being depolymerized using DTT (6.1 mM; 1.1 equiv. w.r.t. end-caps) and DBU (22 mM; 1.0 equiv. w.r.t. end-caps) at rt in CDCl$_3$, the isolated small molecule identified as 1,2,9,10-tetrathiacyclohexadecane by spectral values, and 1,6-hexanedithiol.

NMR spectra

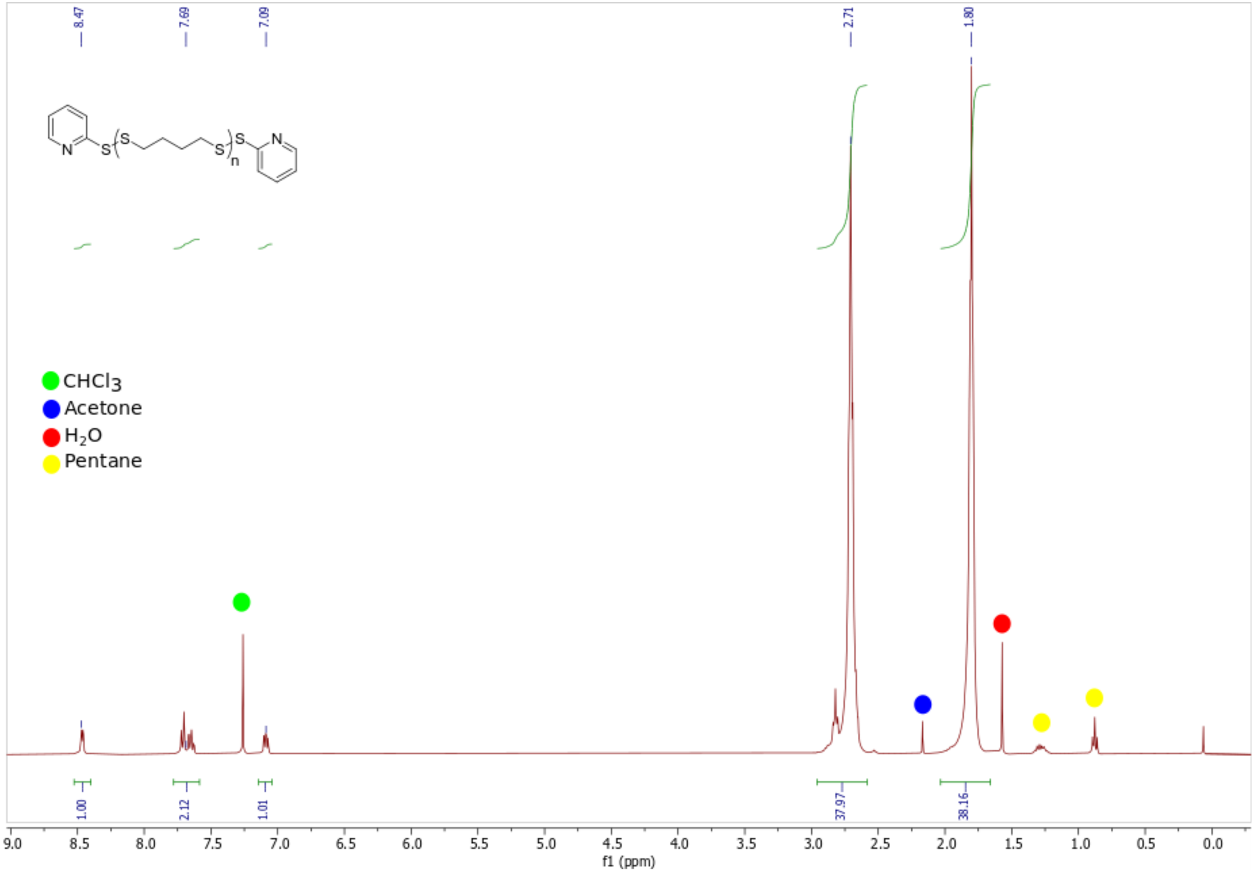


Fig. S16. ^{1}H NMR spectrum of p4-DT$_{10}$ in CDCl$_3$.

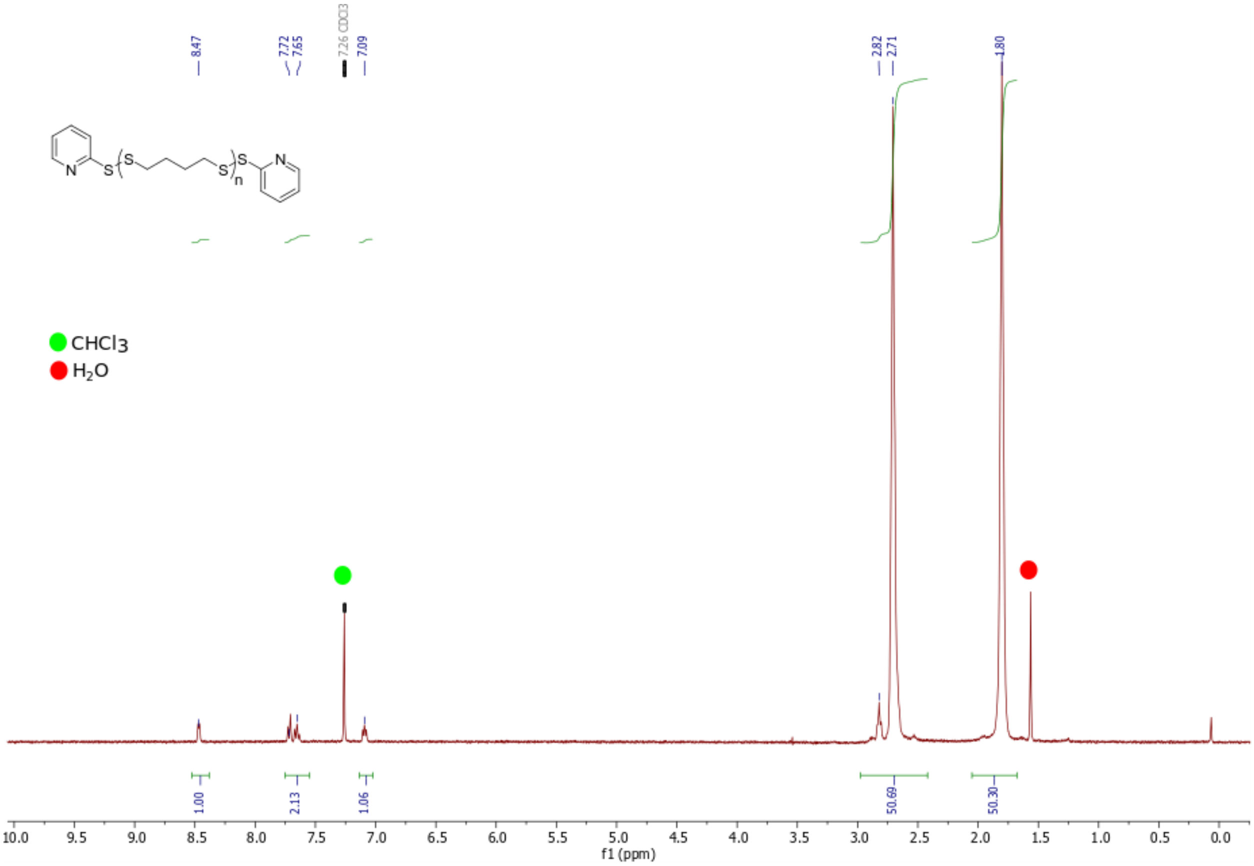


Fig. S17. ^{1}H NMR spectrum of p4-DT$_{20}$ in CDCl$_3$.

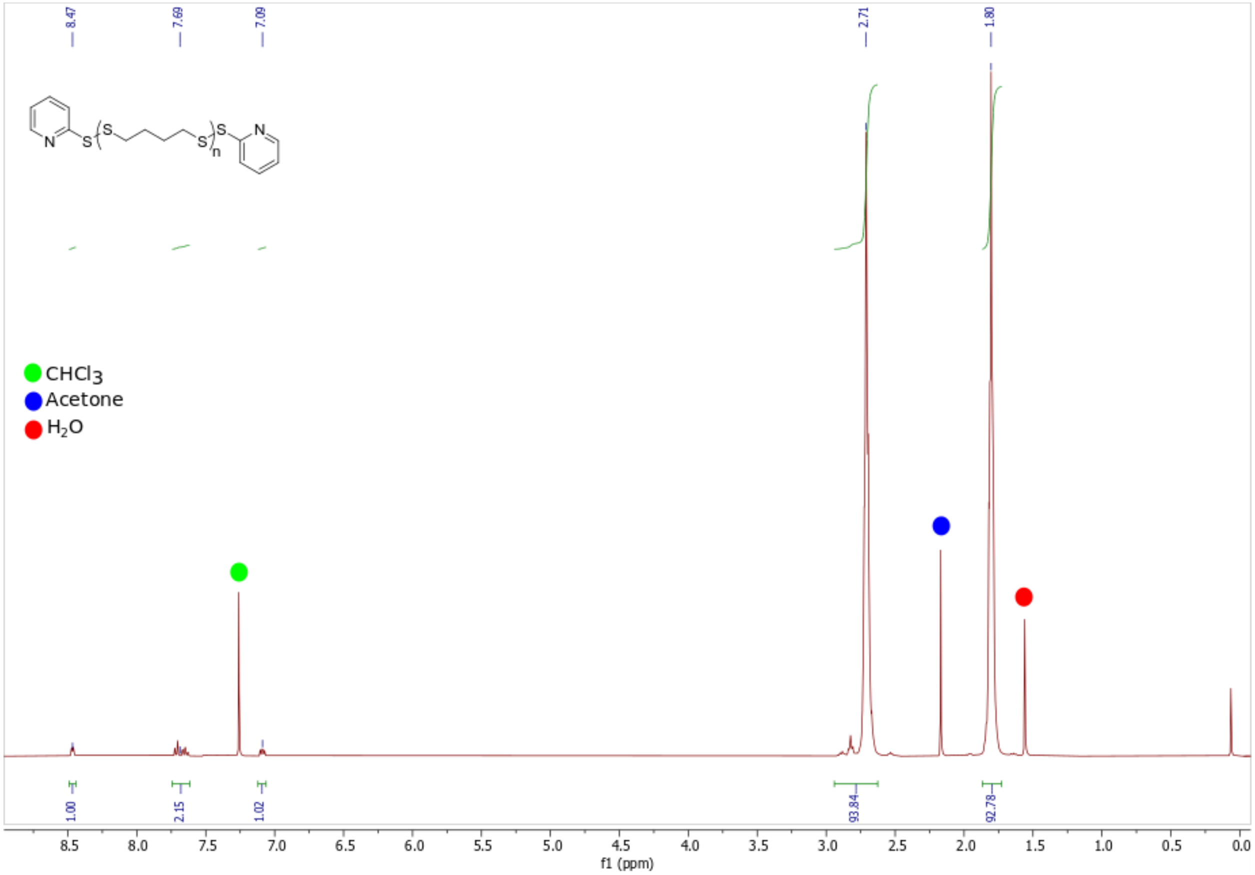


Fig. S18. ^{1}H NMR spectrum of p4-DT$_{40}$ in CDCl$_3$.

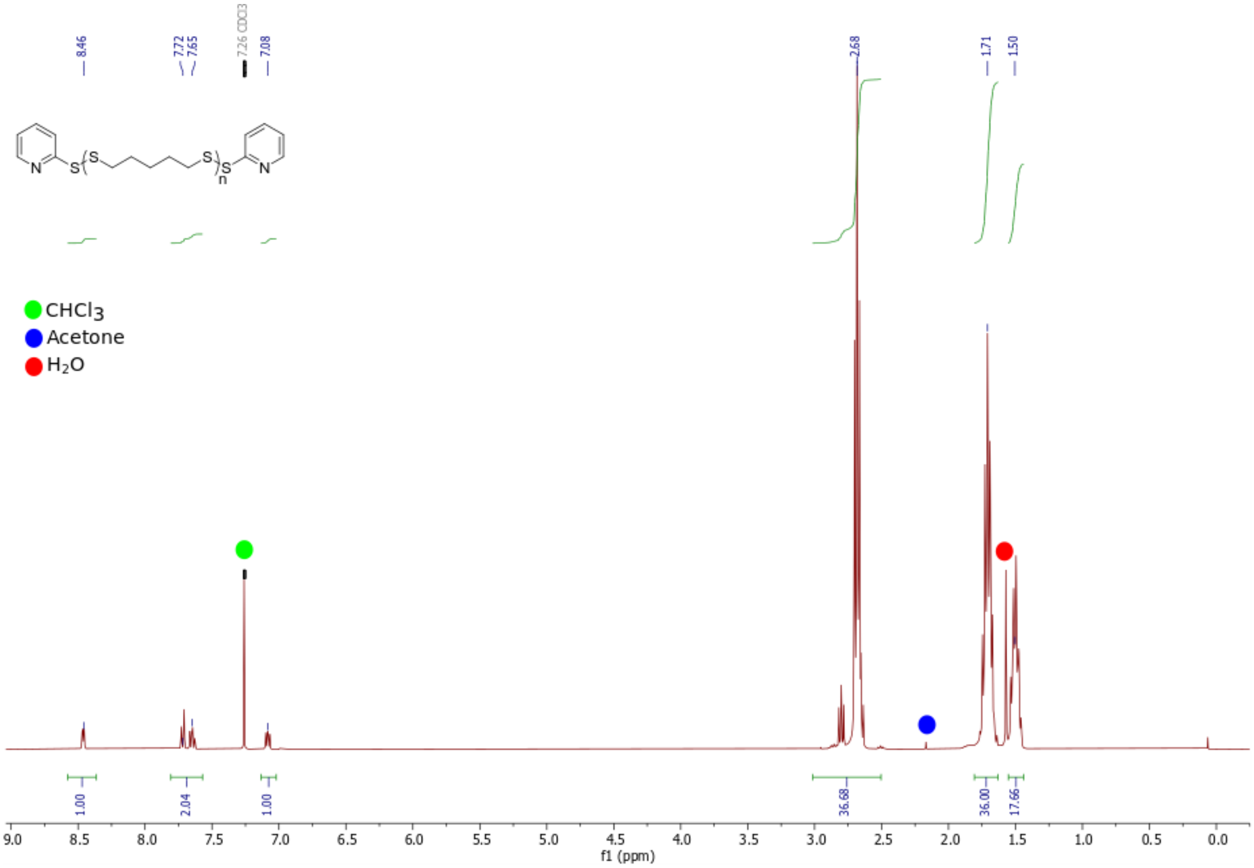


Fig. S19. ^{1}H NMR spectrum of p5-DT$_{10}$ in CDCl$_3$.

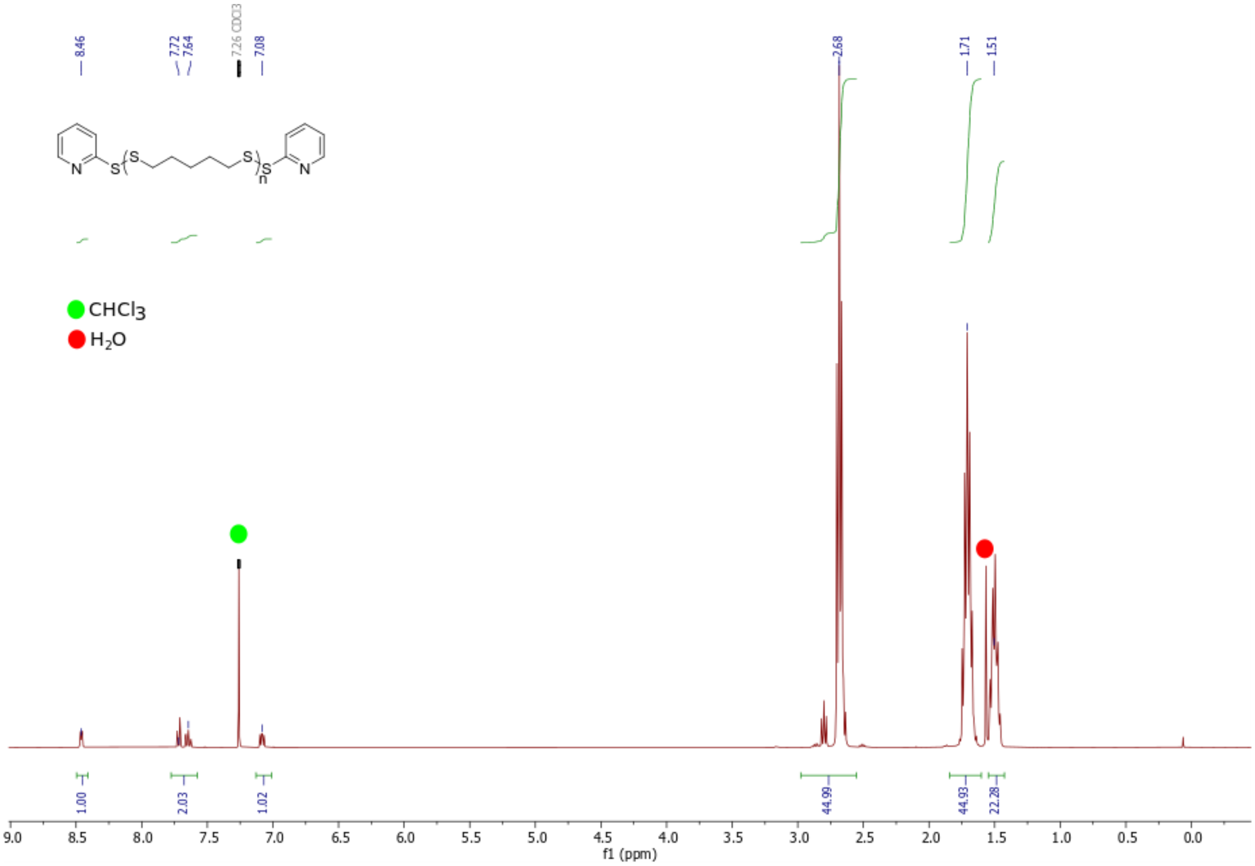


Fig. S20. ^{1}H NMR spectrum of p5-DT$_{20}$ in $CDCl_3$.

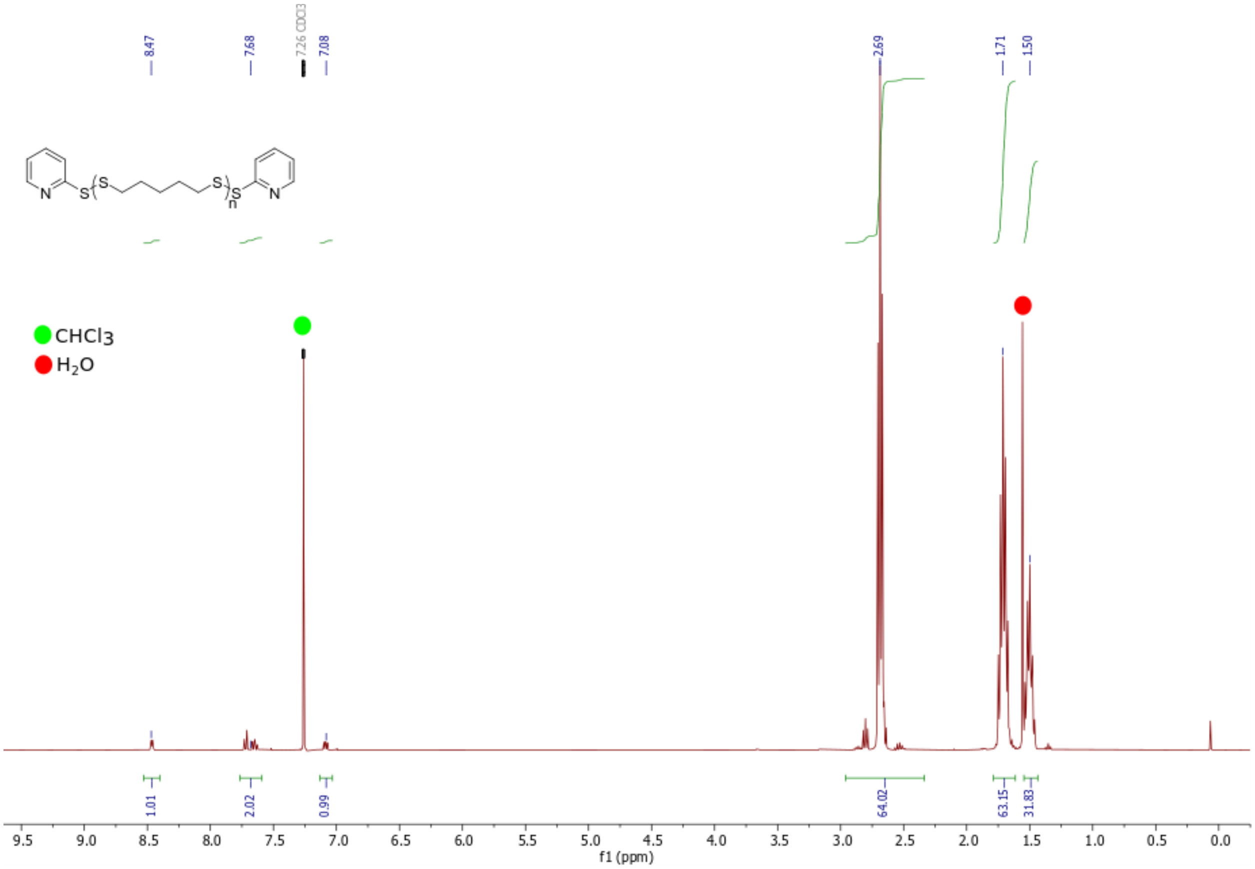


Fig. S21. ^{1}H NMR spectrum of p5-DT$_{40}$ in CDCl$_3$.

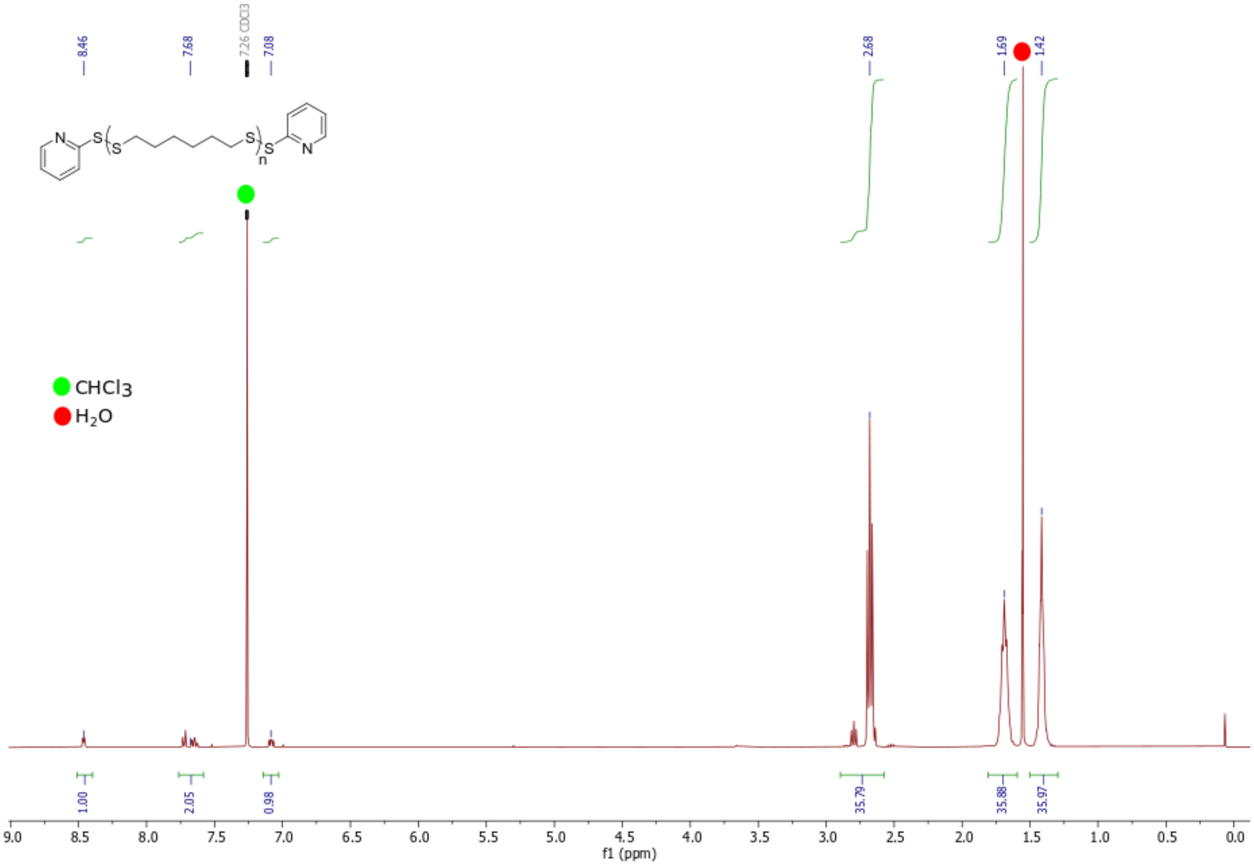


Fig. S22. ^{1}H NMR spectrum of p6-DT$_{10}$ in CDCl$_3$.

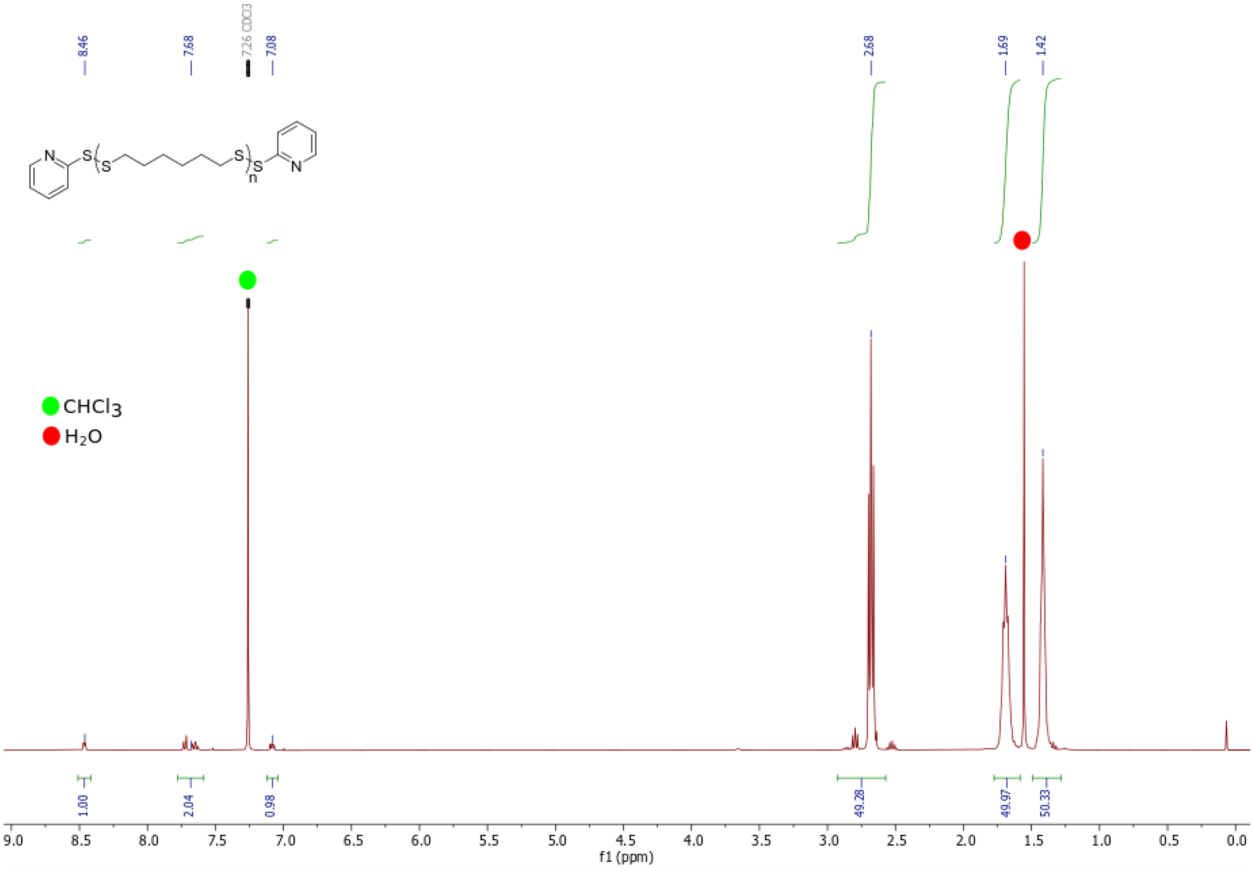


Fig. S23. ^{1}H NMR spectrum of p6-DT$_{20}$ in CDCl$_3$.

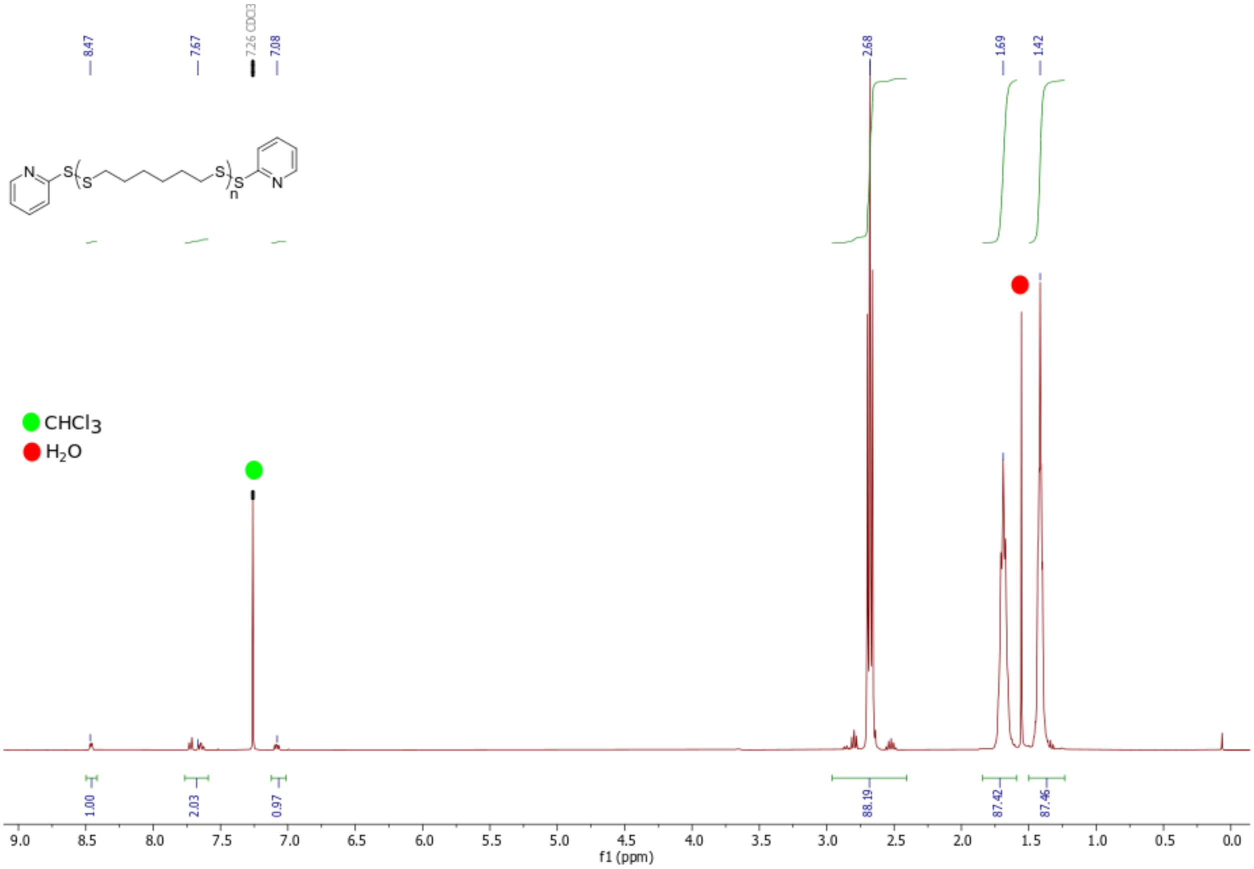


Fig. S24. ^{1}H NMR spectrum of p6-DT$_{40}$ in CDCl$_3$.

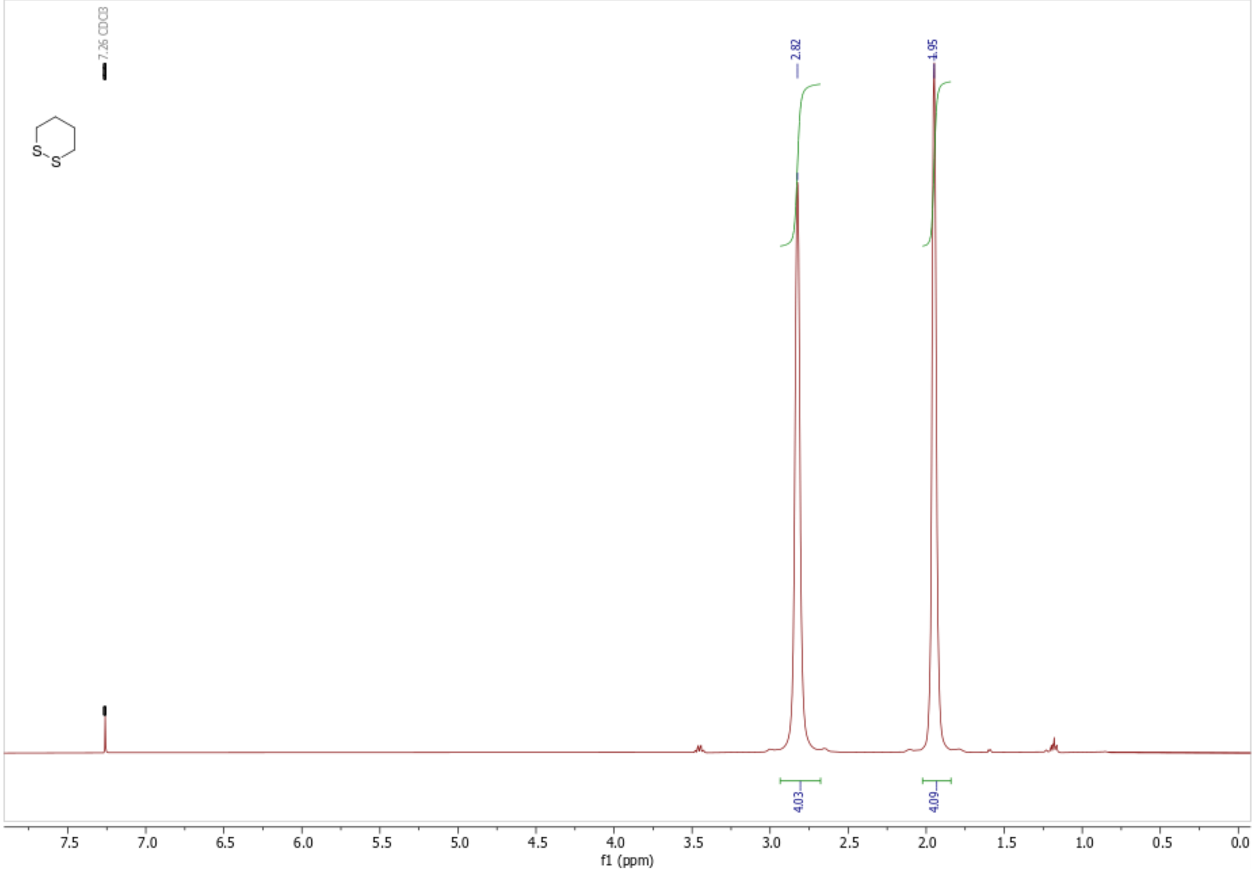


Fig. S25. ^{1}H NMR spectrum of 1,2-dithiane isolated from depolymerization reaction of p4-DT$_{20}$ using DTT (6.9 mM; 1.1 equiv. w.r.t. end-caps) and DBU (6.3 mM; 1.0 equiv. w.r.t. end-caps) at rt in CDCl$_3$.

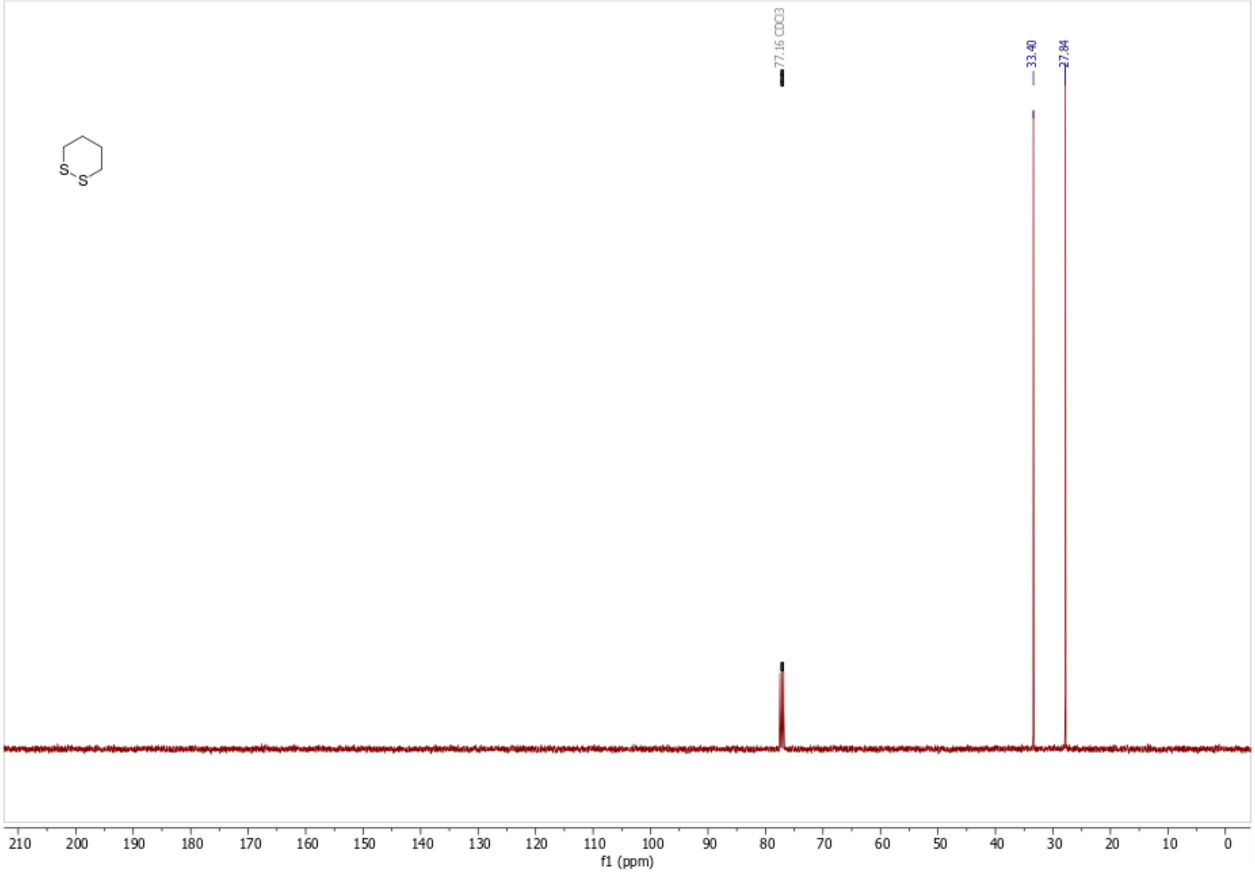


Fig. S26. ^{13}C NMR spectrum of 1,2-dithiane isolated from depolymerization reaction of p4-DT$_{20}$ using DTT (6.9 mM; 1.1 equiv. w.r.t. end-caps) and DBU (6.3 mM; 1.0 equiv. w.r.t. end-caps) at rt in CDCl$_3$.

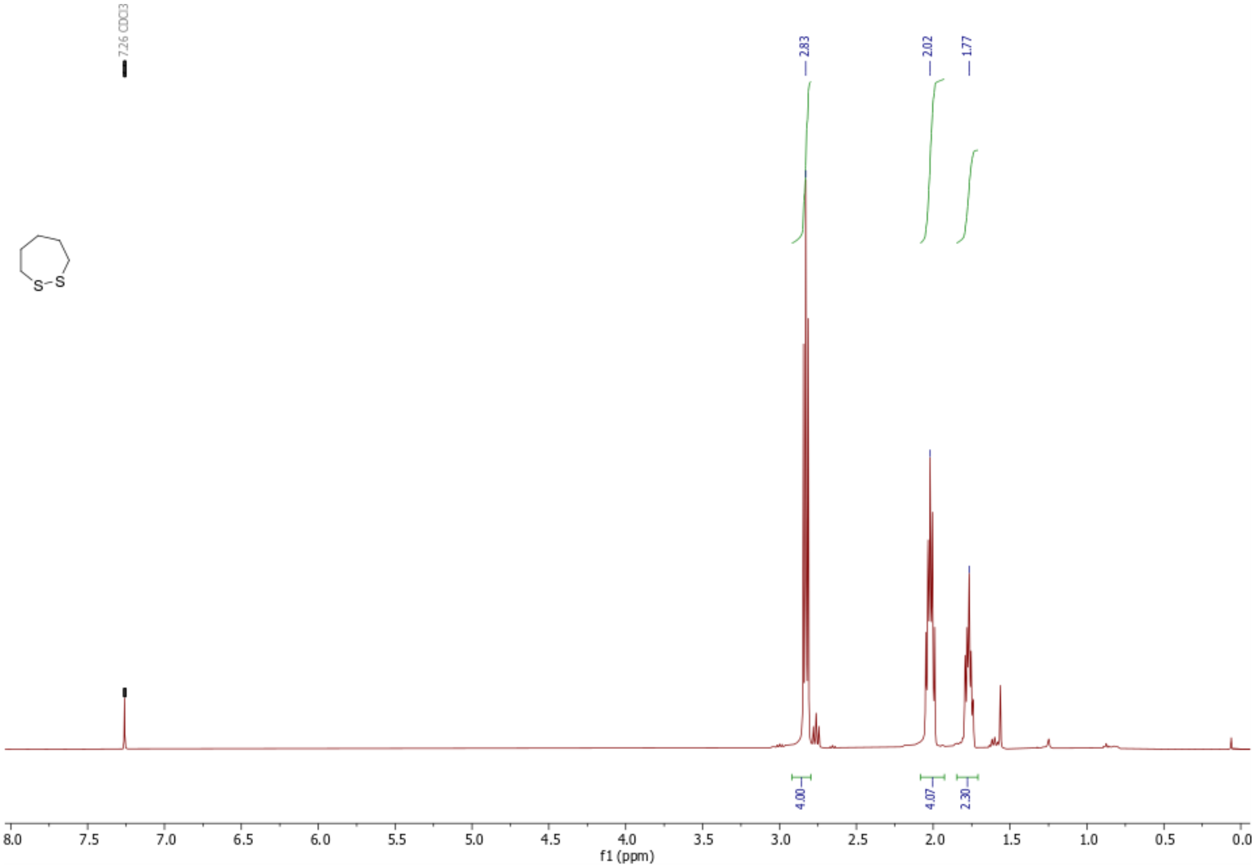


Fig. S27. ^{1}H NMR spectrum of 1,2-dithiepane isolated from depolymerization reaction of p5-DT$_{20}$ using DTT (6.9 mM; 1.1 equiv. w.r.t. end-caps) and DBU (25 mM; 4.0 equiv. w.r.t. end-caps) at rt in CDCl$_3$.

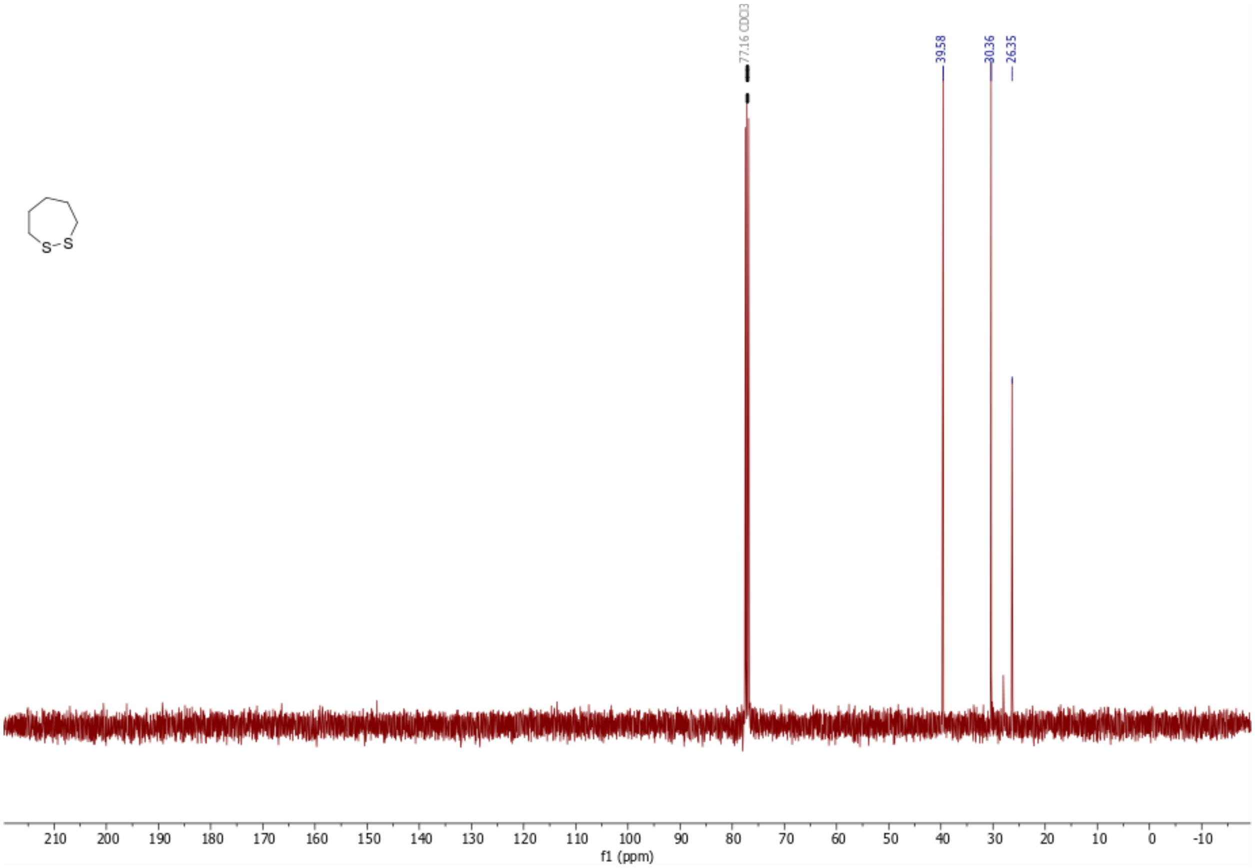


Fig. S28. ^{13}C NMR spectrum of 1,2-dithiepane isolated from depolymerization reaction of p5-DT$_{20}$ using DTT (6.9 mM; 1.1 equiv. w.r.t. end-caps) and DBU (25 mM; 4.0 equiv. w.r.t. end-caps) at rt in CDCl$_3$.

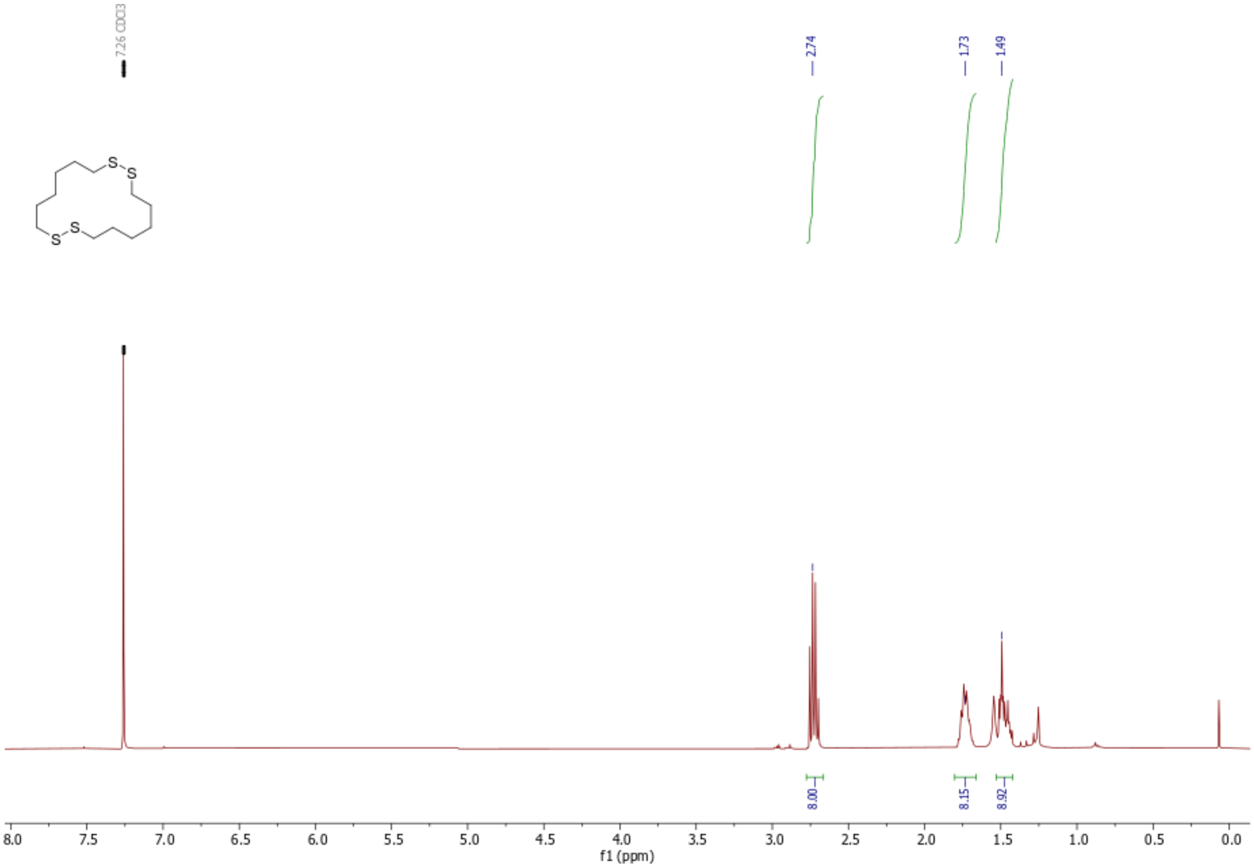


Fig. S29. ^{1}H NMR spectrum of 1,2,9,10-tetrathiacyclohexadecane isolated from depolymerization reaction of p6-DT$_{20}$ using DTT (6.1 mM; 1.1 equiv. w.r.t. end-caps) and DBU (22 mM; 4.0 equiv. w.r.t. end-caps) at rt in CDCl$_3$.

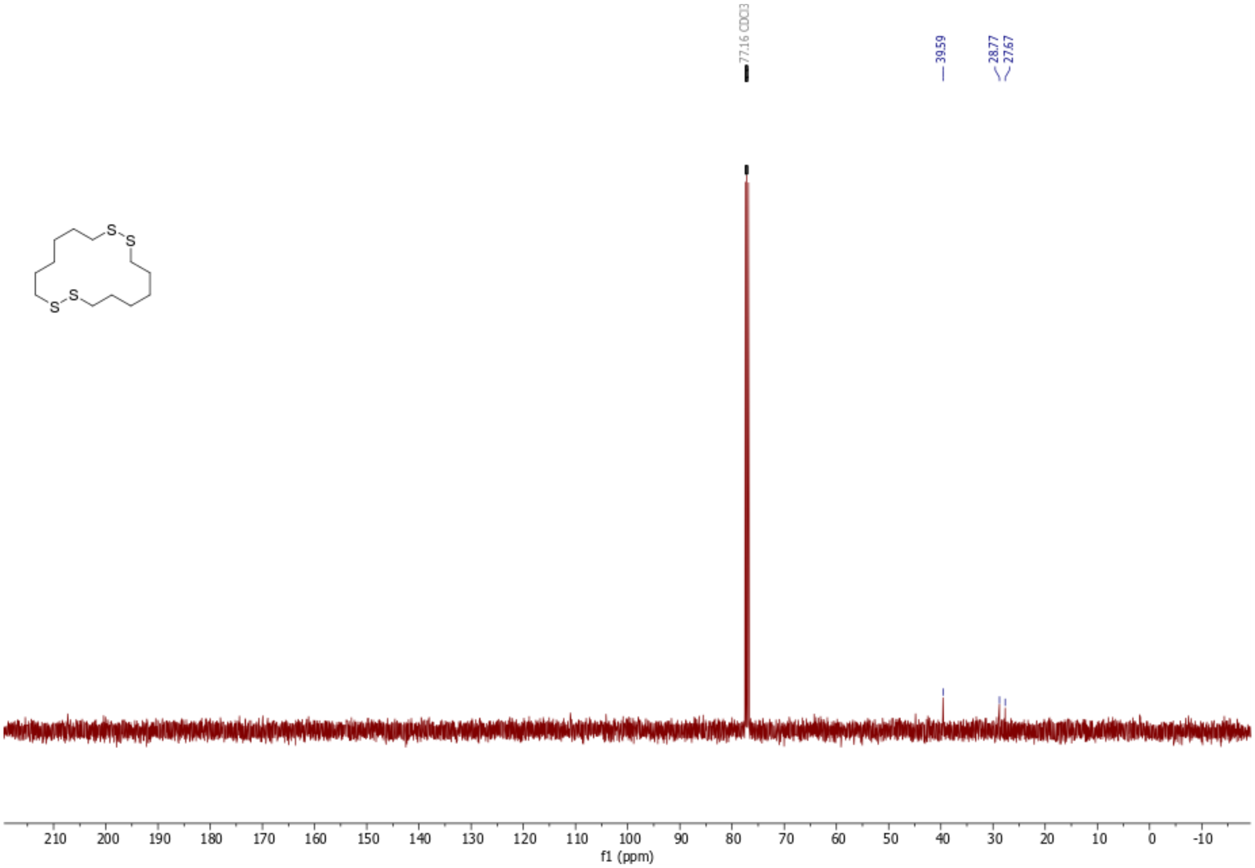


Fig. S30. ^{13}C NMR spectrum of 1,2,9,10-tertathiacyclohexadecane isolated from depolymerization reaction of p6-DT$_{20}$ using DTT (6.1 mM; 1.1 equiv. w.r.t. end-caps) and DBU (22 mM; 4.0 equiv. w.r.t. end-caps) at rt in CDCl$_3$.

GPC traces

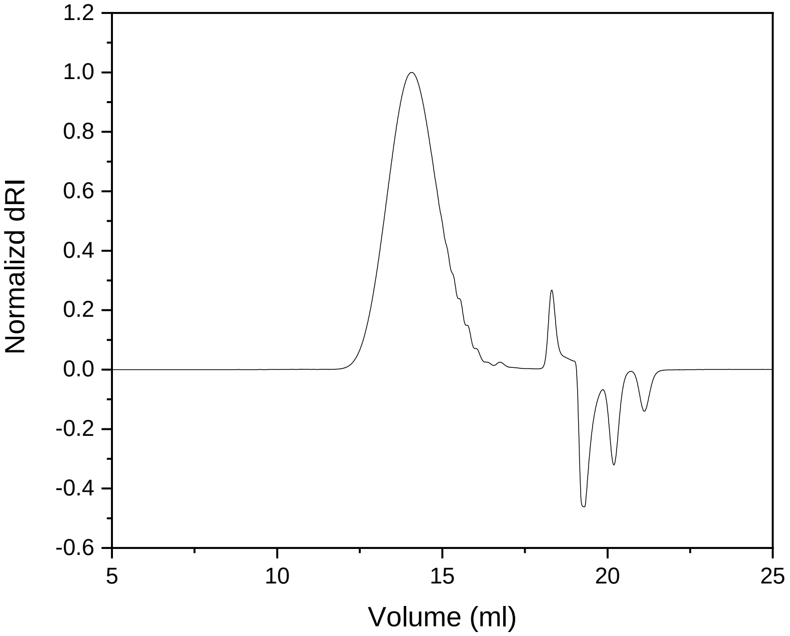


Fig. S31. GPC trace of p4-DT_{10} in THF.

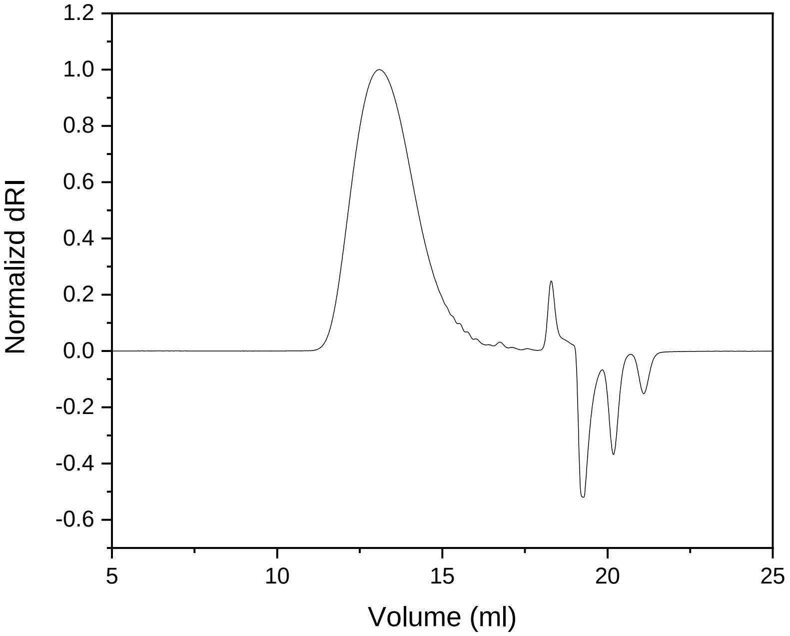


Fig. S32. GPC trace of p4-DT_{20} in THF.

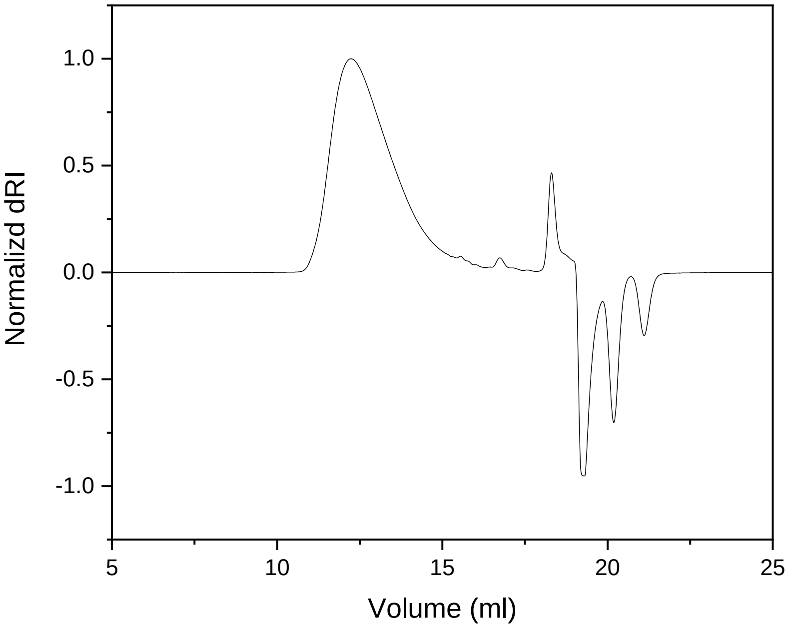


Fig. S33. GPC trace of p4-DT_{40} in THF.

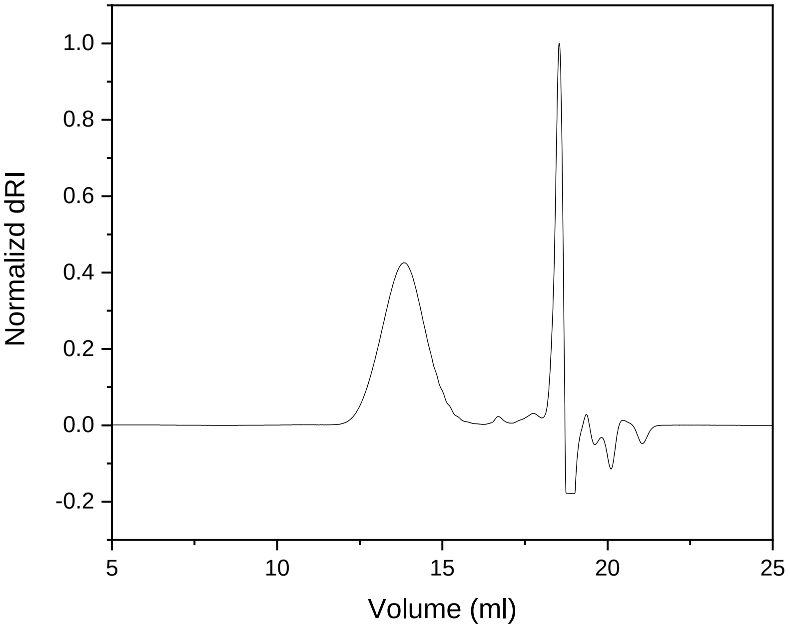


Fig. S34. GPC trace of p5-DT_{10} in THF.

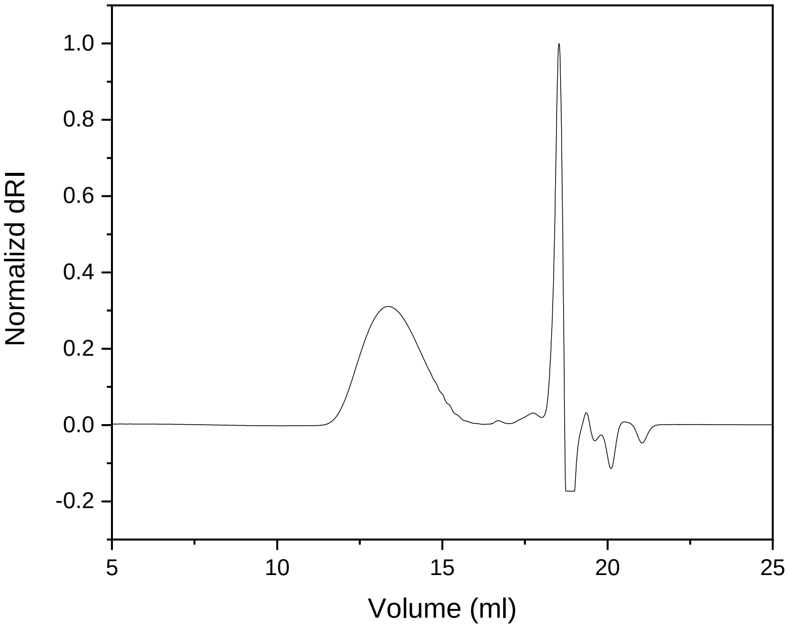


Fig. S35. GPC trace of p5-DT$_{20}$ in THF.

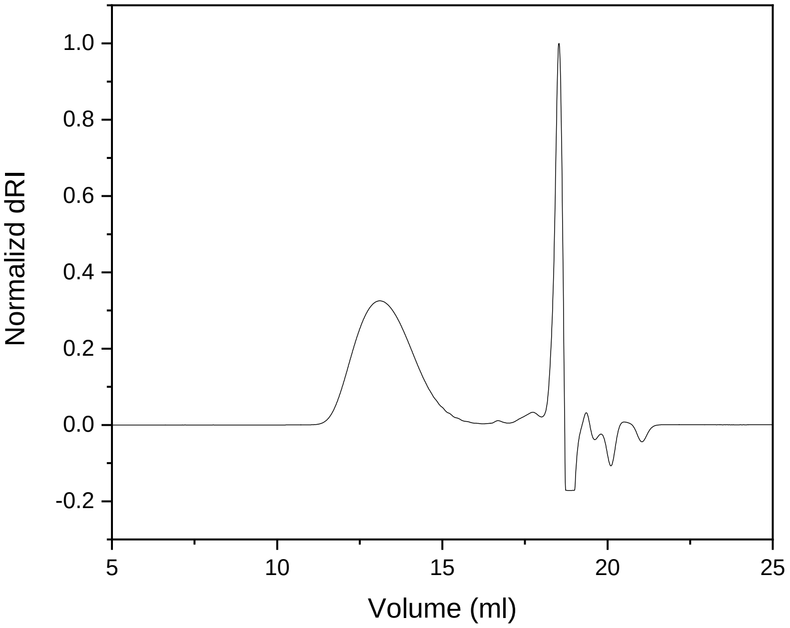


Fig. S36. GPC trace of p5-DT$_{40}$ in THF.

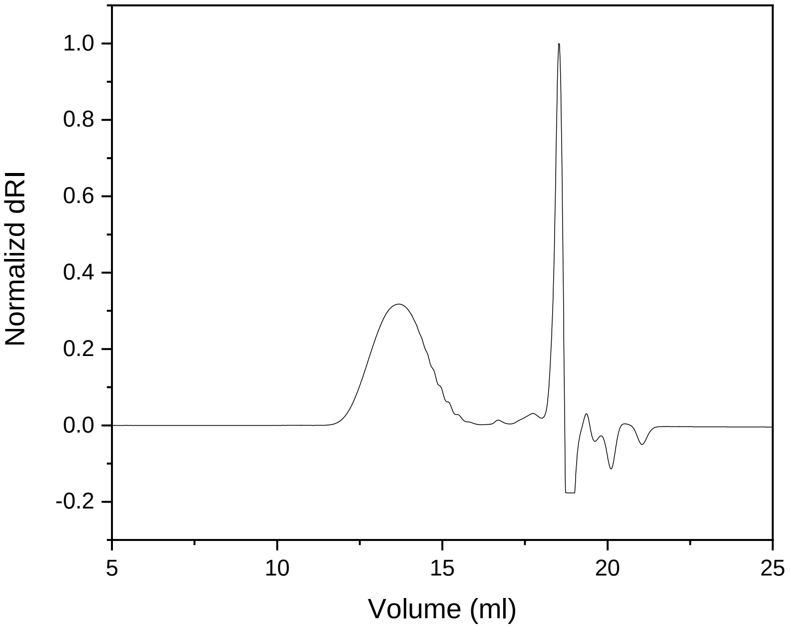


Fig. S37. GPC trace of p6-DT$_{10}$ in THF.

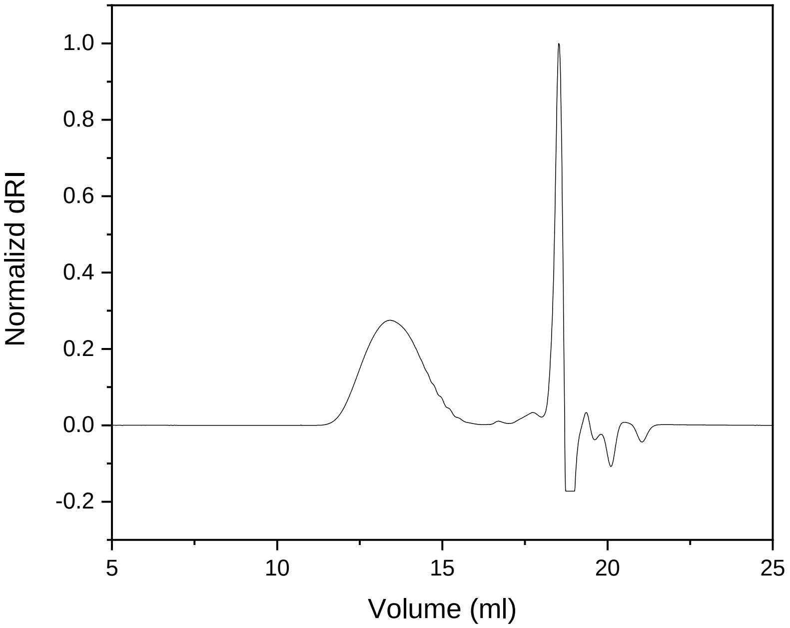


Fig. S38. GPC trace of p6-DT$_{20}$.

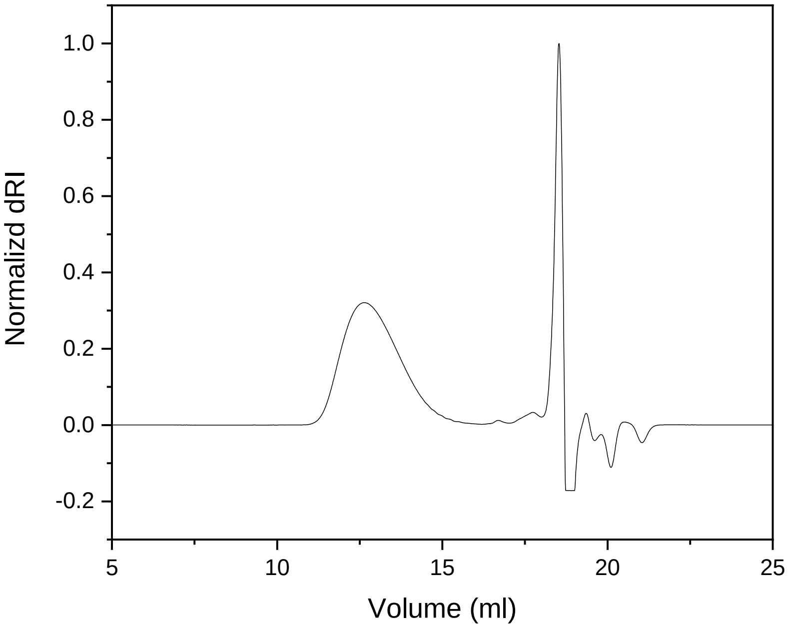


Fig. S39. GPC trace of p6-DT$_{40}$ in THF.

DSC thermograms

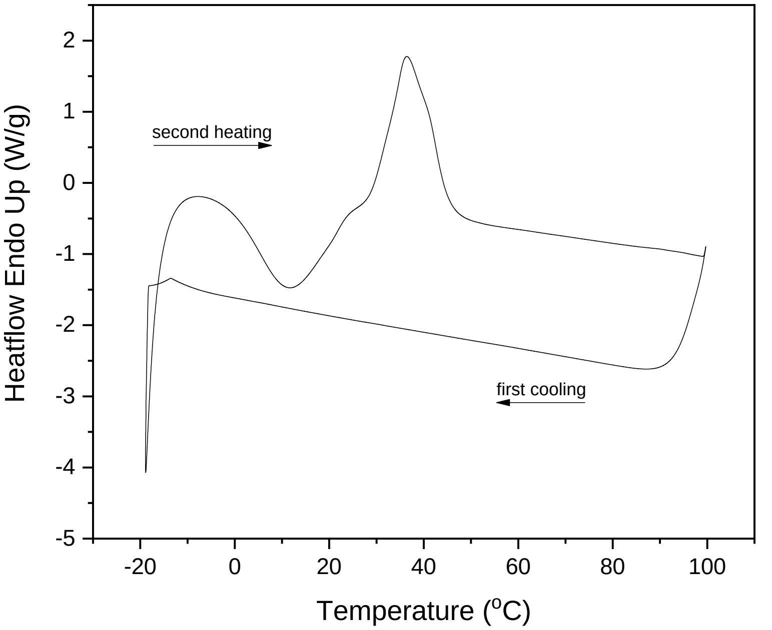


Fig. S40. DSC trace of p4-DT$_{10}$.

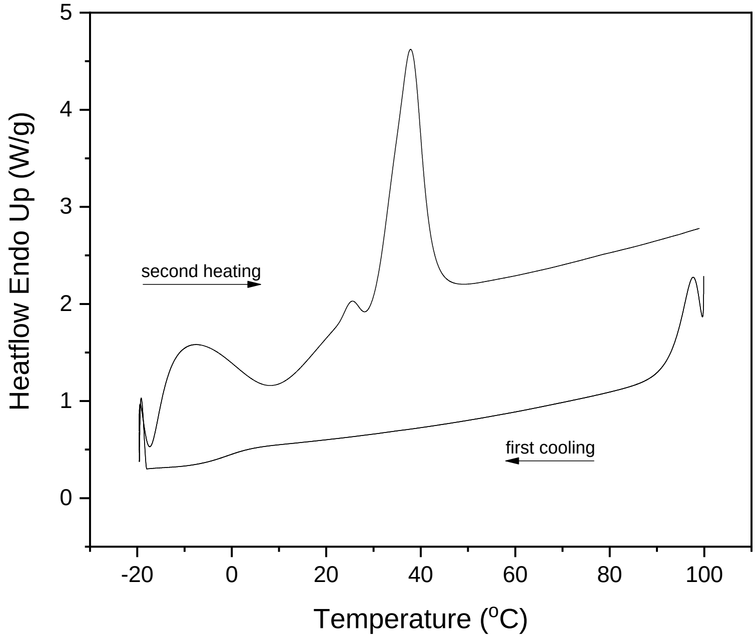


Fig. S41. DSC trace of p4-DT$_{20}$.

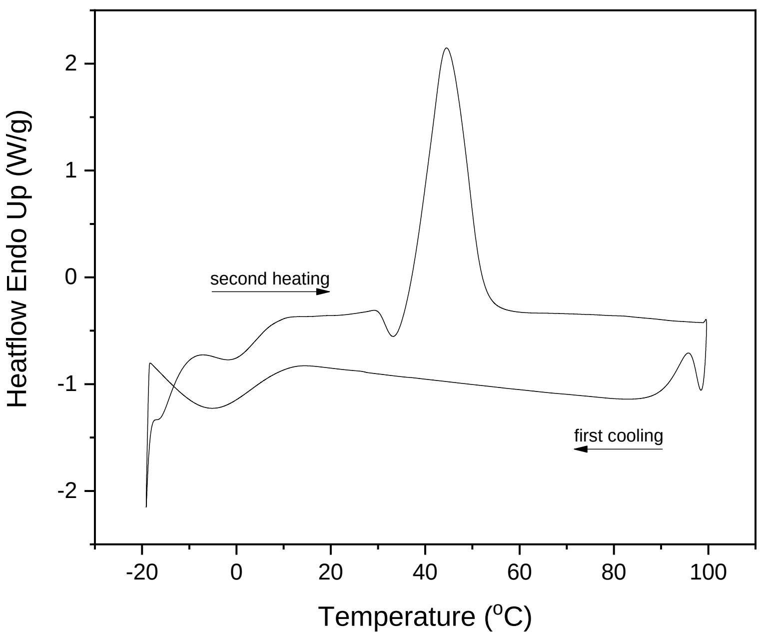


Fig. S42. DSC trace of p4-DT$_{40}$.

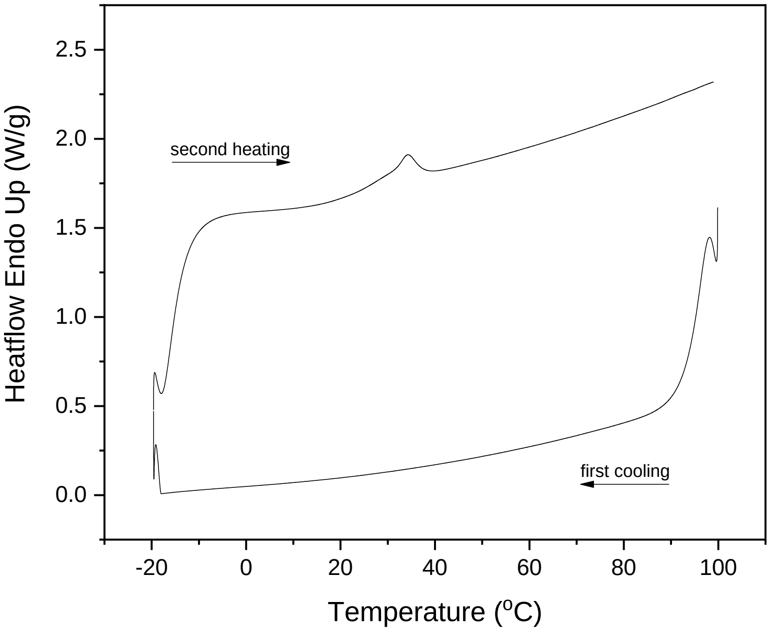


Fig. S43. DSC trace of p5-DT$_{10}$.

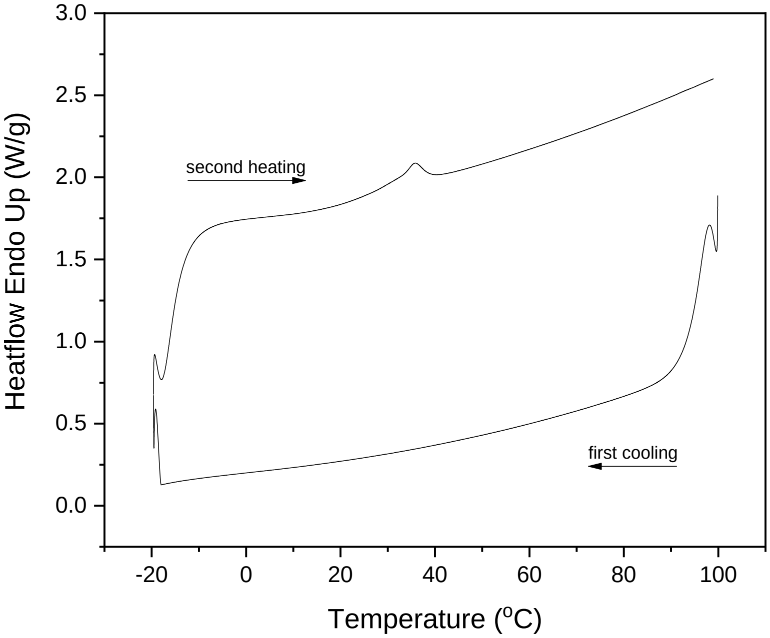


Fig. S44. DSC trace of p5-DT$_{20}$.

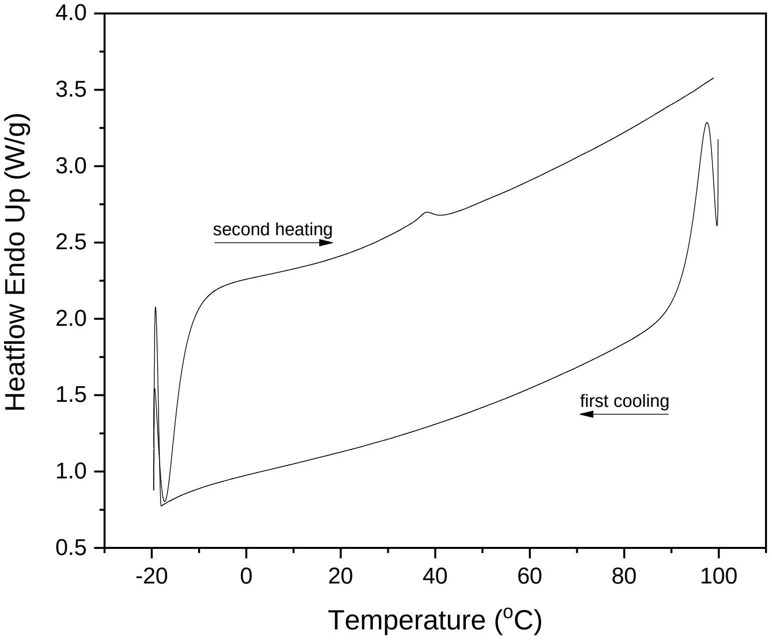


Fig. S45. DSC trace of p5-DT$_{40}$.

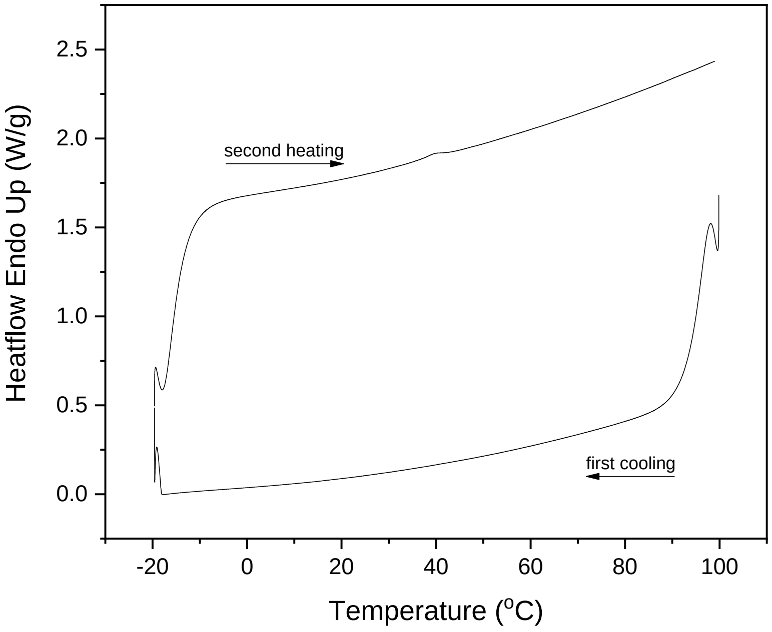


Fig. S46. DSC trace of p6-DT$_{10}$.

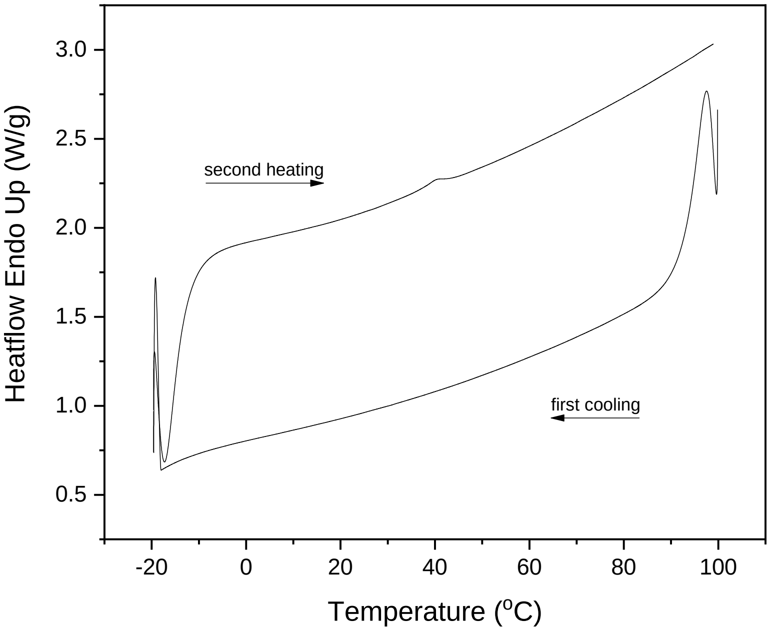


Fig. S47. DSC trace of p6-DT$_{20}$.

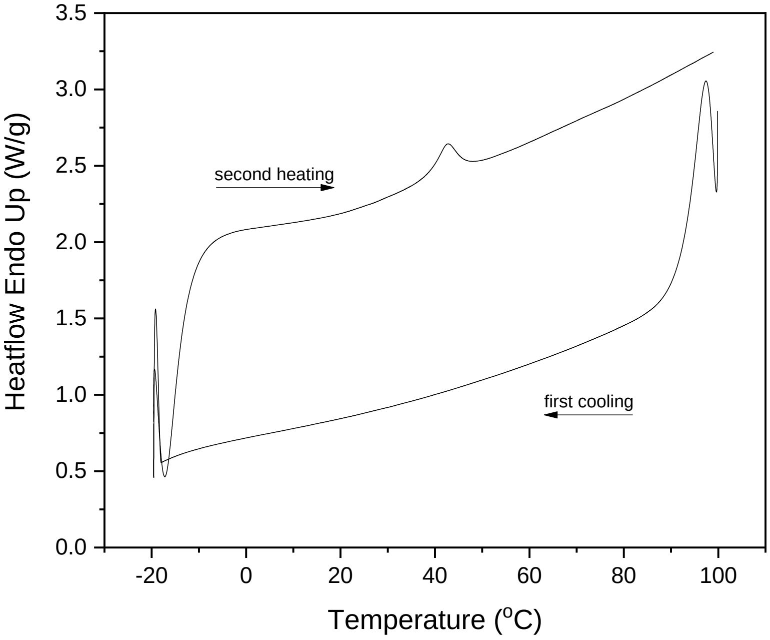


Fig. S48. DSC trace of p6-DT$_{40}$.

References

S1. D. Basak, R. Kumar and S. Ghosh, *Macromol. Rapid Commun.*, 2014, **35**, 1340–1344.

S2. H. Abul-Futouh, L. R. Almazahreh, M. K. Harb, H. Gorls, M. El-Khateeb and W. Weigand, *Inorg. Chem.*, 2017, **56**, 10437–10451.