

## Supporting Information

for

### Cyclic Thioanhydride/Episulfide Copolymerizations by Bipyridine-Bisphenolate Aluminum/Onium Pair: Approach to Structurally and Functionally Diverse Poly(thioester)s

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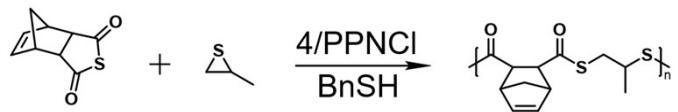
\* Corresponding authors: [binwang@tju.edu.cn](mailto:binwang@tju.edu.cn) (B.W.)

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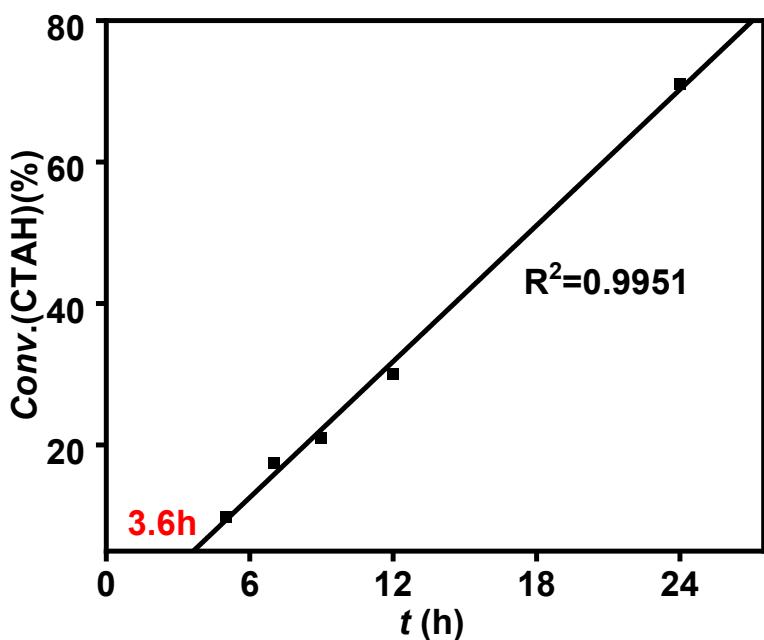
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**Table S1.** The copolymerization of CTAH and PS at different CTA equivalents.

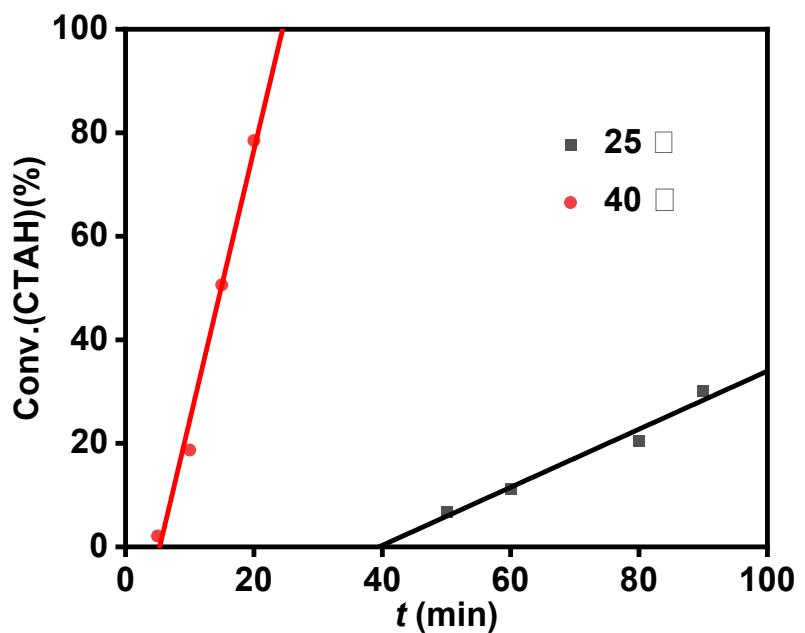


Entry <sup>a</sup>	CTA/Cat.	T(°C)	t(min)	Conv.(%) <sup>b</sup>	$M_{n,\text{theo}}(\text{kDa})^c$	$M_n(\text{kDa})^d$	$D^d$
1	5	25	50	94.1	5.9	13.9	1.20
2	10	25	25	85.5	2.7	6.2	1.16
3	20	25	30	83.0	1.3	3.0	1.16
4	50	25	30	97.4	0.6	1.2	1.20
5	100	25	30	74.8	0.2	0.7	1.24

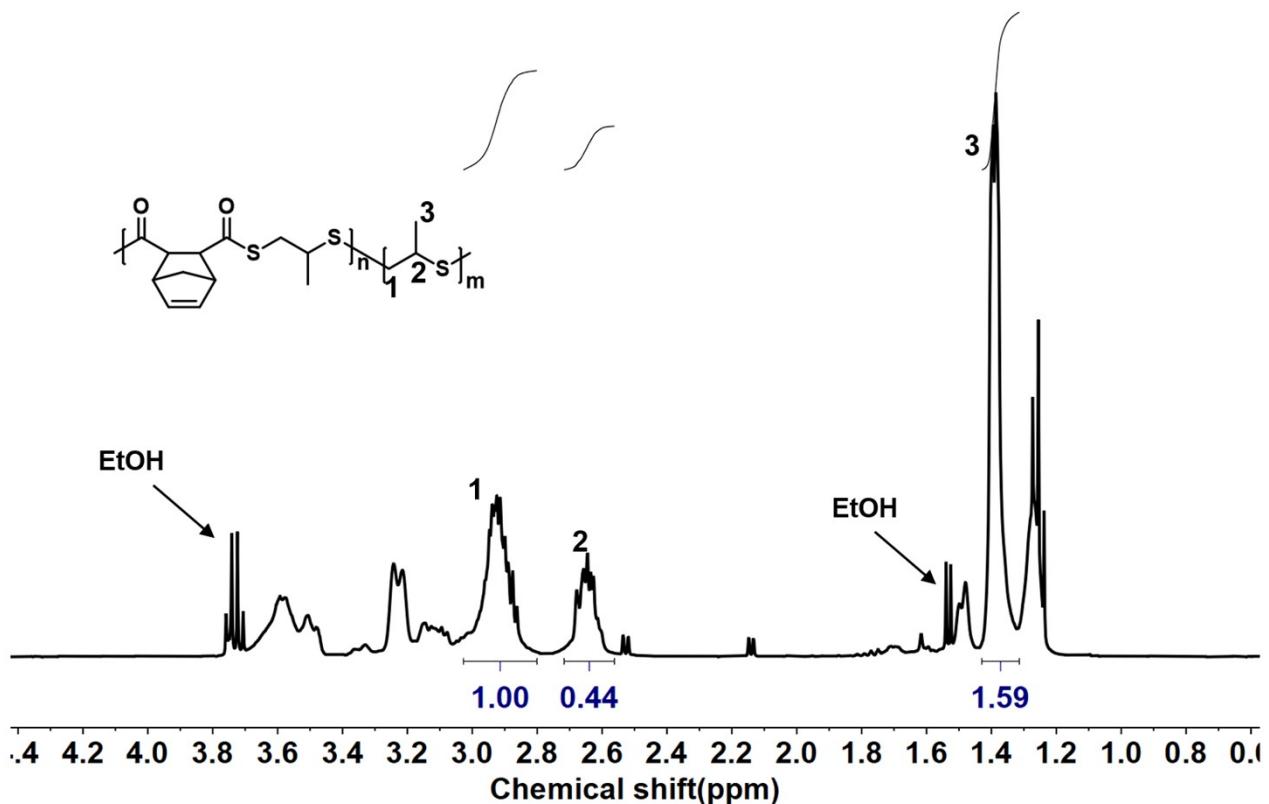
<sup>a</sup> Unless other stated, the polymerizations were conducted in bulk at 25 °C, [PS]:[CTA]:[Lewis acid]:[Lewis base] = 1000/250/1/1. <sup>b</sup> Conversion of CTAH was determined by <sup>1</sup>H NMR. <sup>c</sup> The theoretical molecular weight was calculated based on the assumption that each Al center initiated two polymer chains.  $M_{n,\text{theo}} = [M_{\text{CTAH}} + M_{\text{PS}}] \times 250 \times \text{conv} (\%) \times 0.5 \div \text{CTA/Cat}$ . <sup>d</sup> Number-averaged molecular weight ( $M_n$ ) and polydispersity ( $D$ ) were determined by GPC and referenced by polystyrene standards. The  $M_{n,\text{GPC}}$  was not corrected.



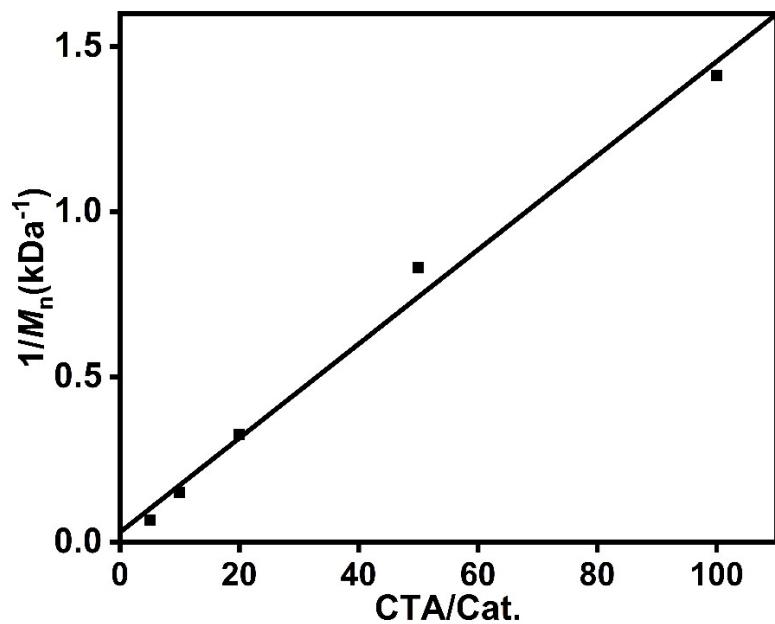
**Figure S1.** Kinetic plots of the copolymerization of CTAH and PS in toluene at 25 °C (Conditions: CTAH:PS:**4**:PPNCl = 250:250:1:1 in toluene, [PS] = 2.5 mol/L).



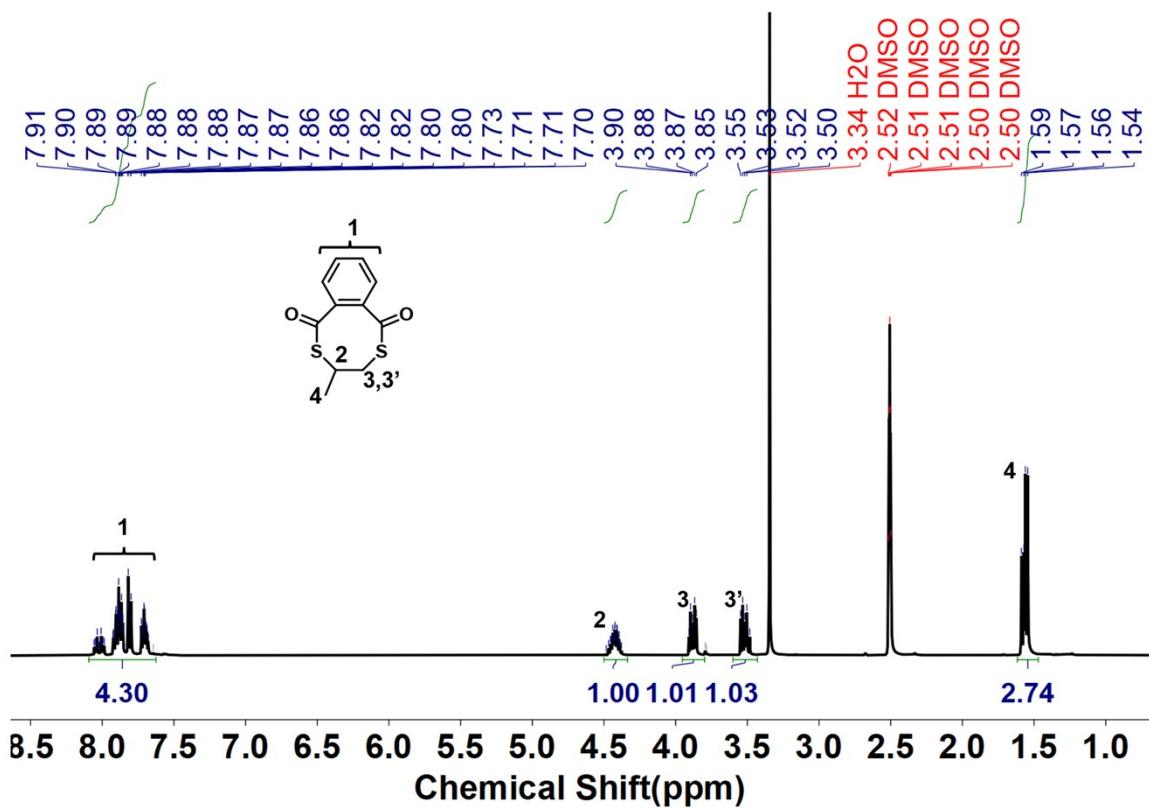
**Figure S2.** Kinetic plots of the copolymerization of CTAH and PS at 25 °C and 40 °C.



**Figure S3.** The copolymer obtained by copolymerization of CTAH and PS at 40 °C.



**Figure S4.** The relationship between CTA/Cat. and  $M_n$ .



**Figure S5.**  $^1\text{H}$  NMR spectrum of 8-membered cyclic molecules in DMSO.

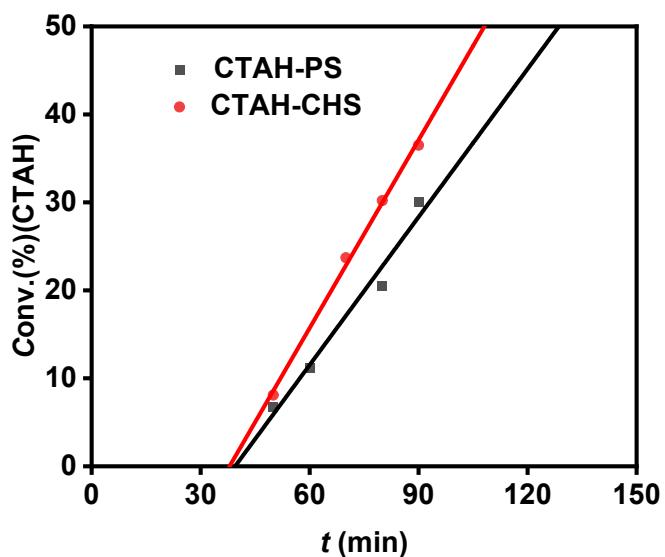


Figure S6. Kinetics of CTAH/PS copolymerisation with CTAH/CHS.

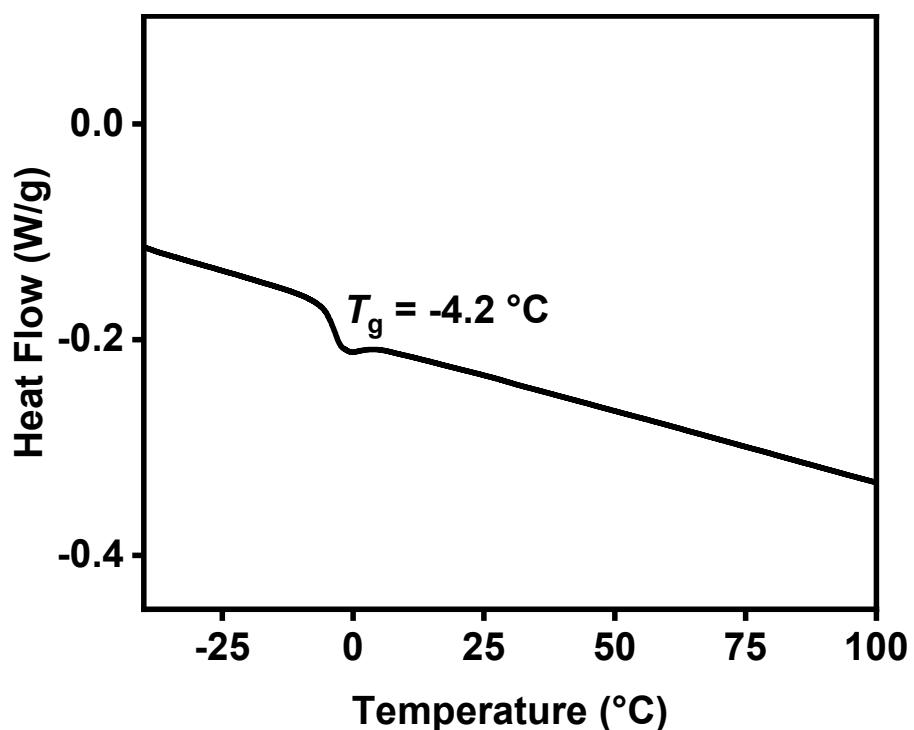
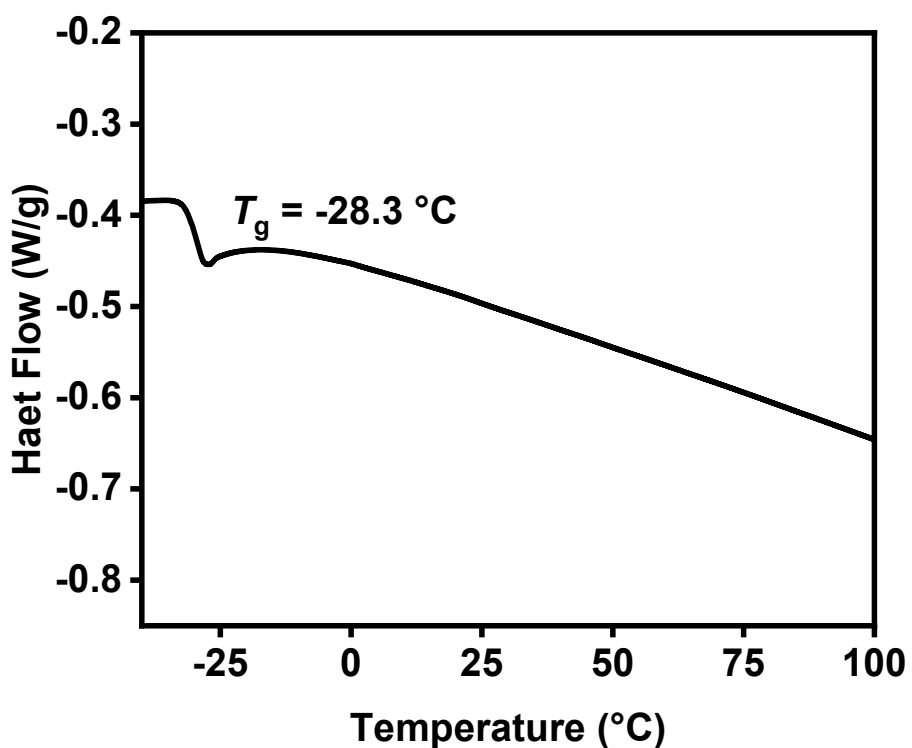
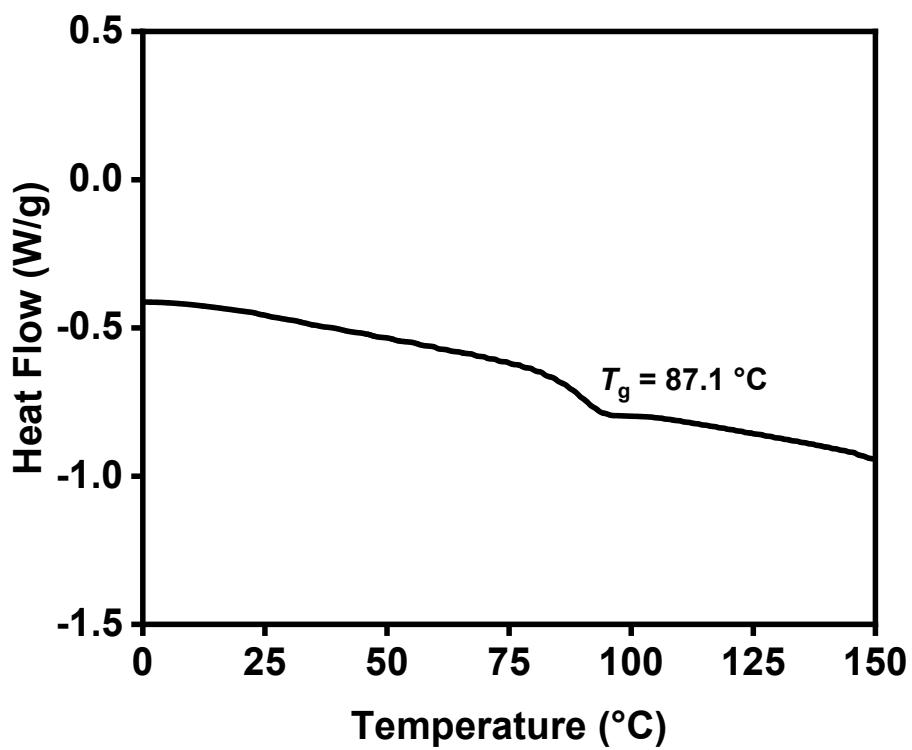


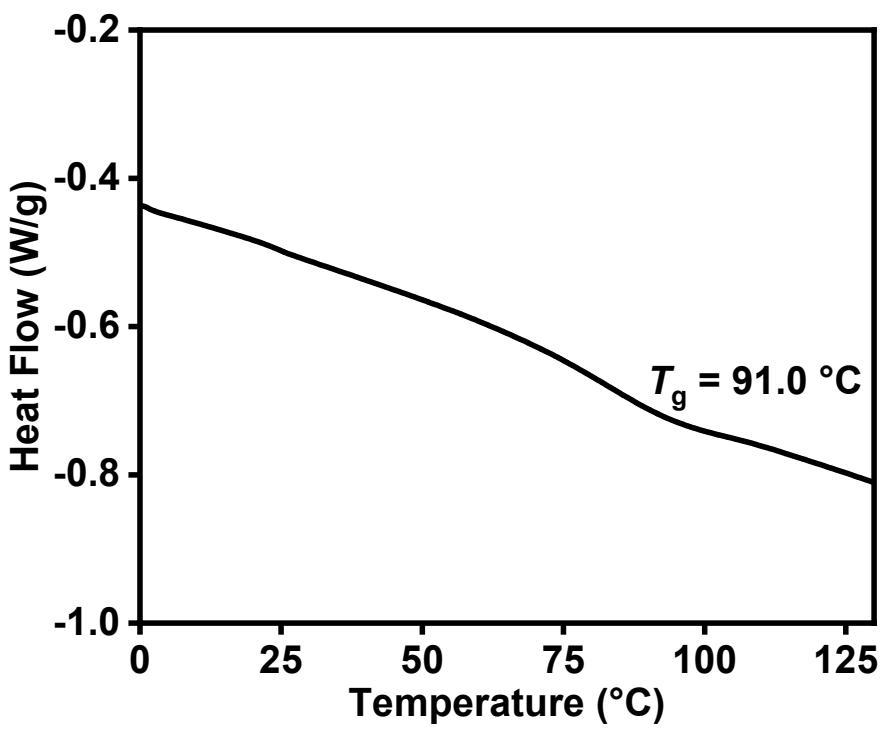
Figure S7. DSC thermogram of the poly(STAH-*alt*-PS).



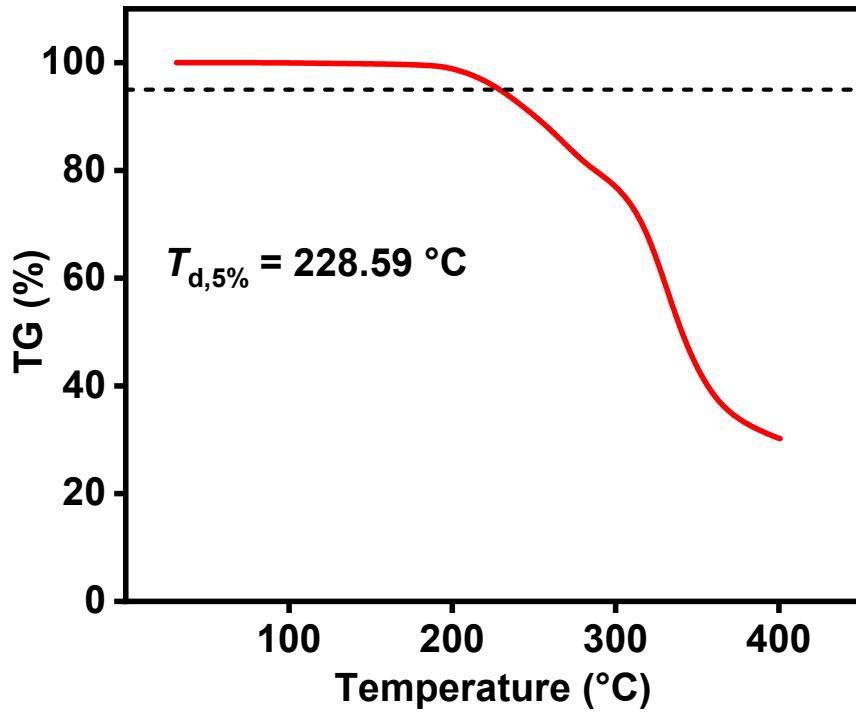
**Figure S8.** DSC thermogram of the poly(GTAH-*alt*-PS).



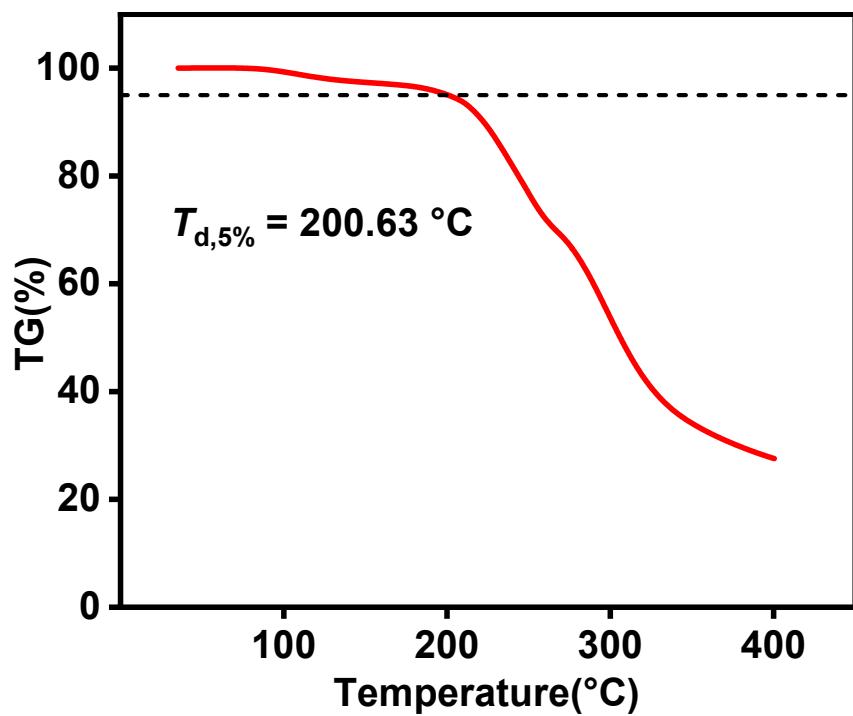
**Figure S9.** DSC thermogram of the poly(CTAH-*alt*-PS).



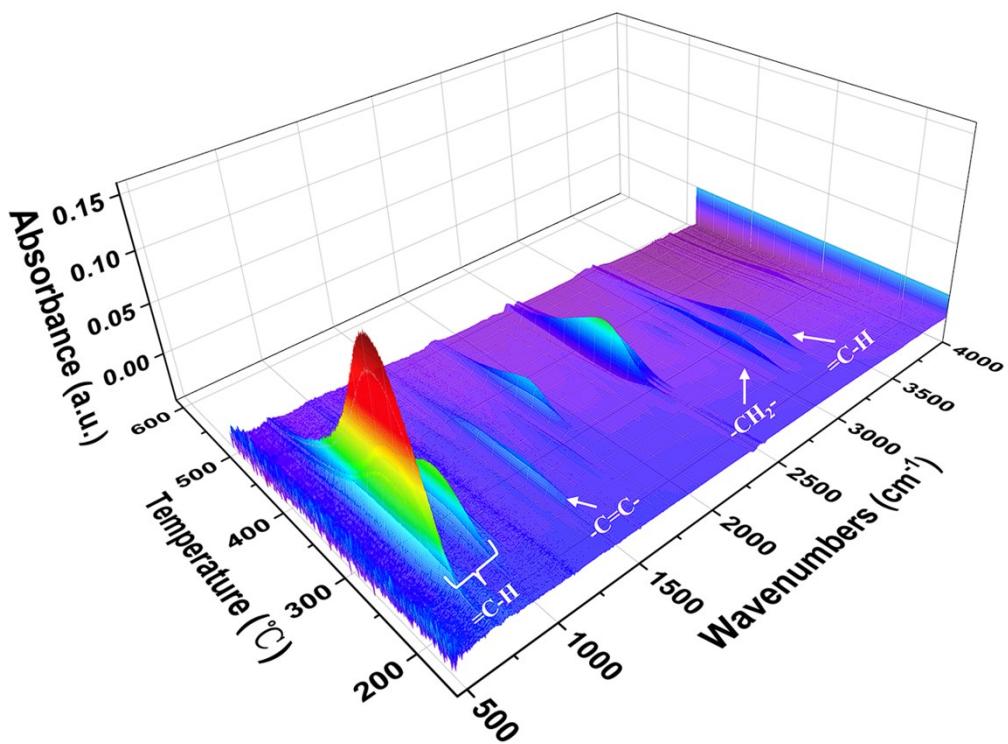
**Figure S10.** DSC thermogram of the poly(CTAH-*alt*-CHS).



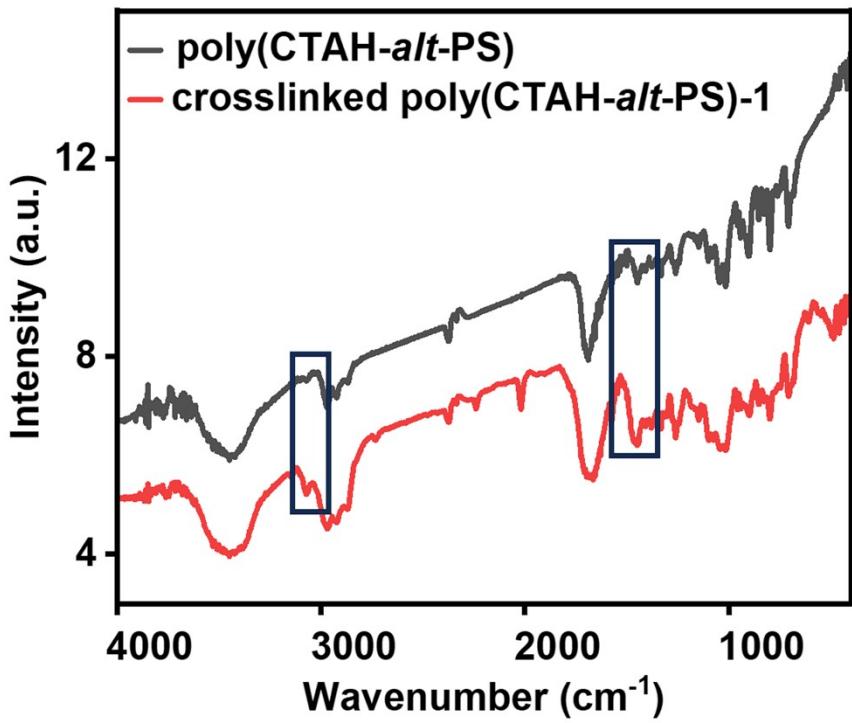
**Figure S11.** TGA curve of poly(CTAH-*alt*-PS).



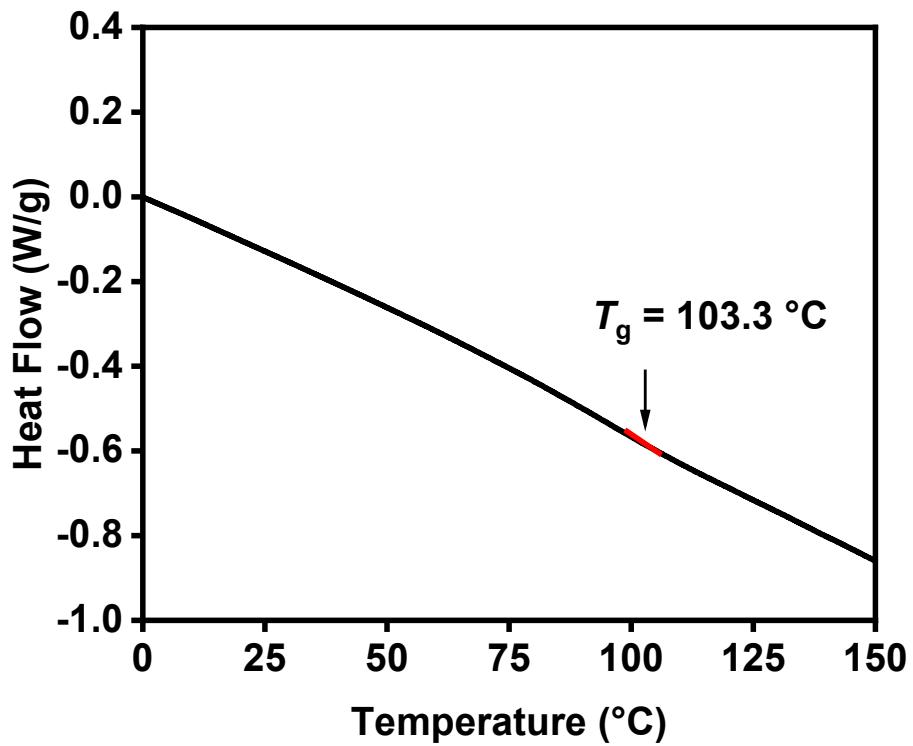
**Figure S12.** TGA curve of poly(CTAH-*alt*-CHS).



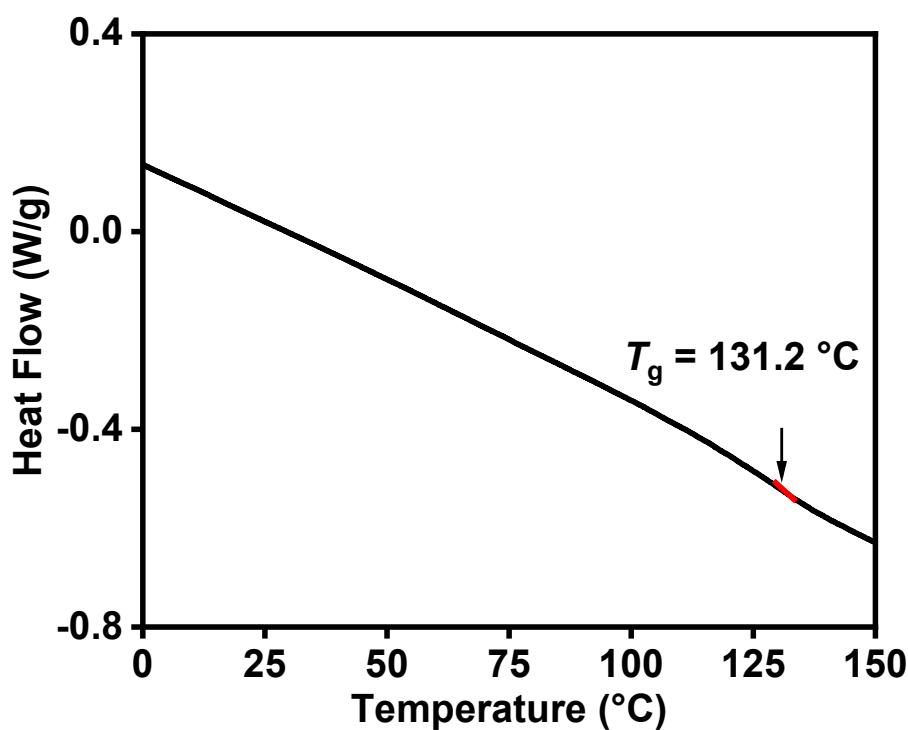
**Figure S13.** The TG-IR analysis of the poly(CTAH-*alt*-PS).



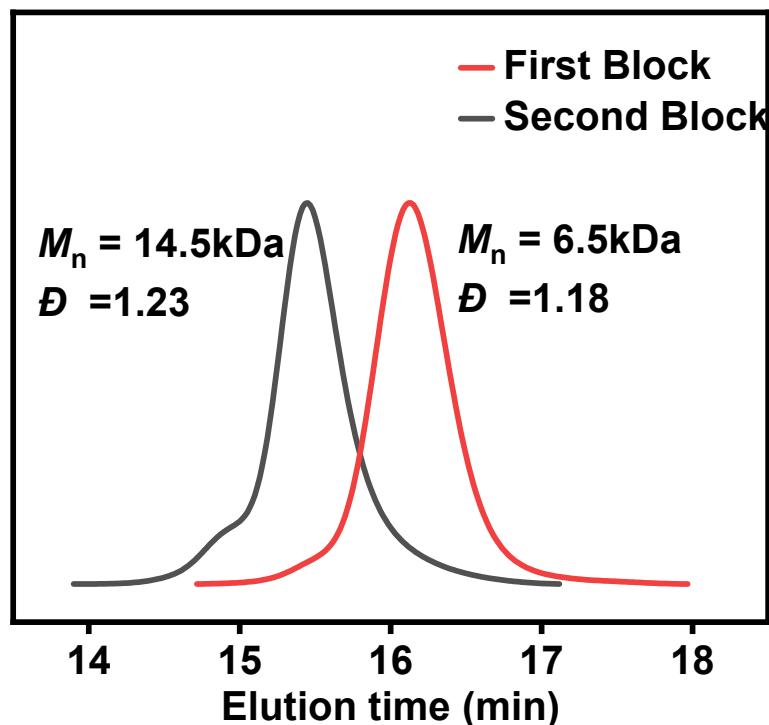
**Figure S14.** The FT-IR analysis of the poly(CTAH-*alt*-PS) and crosslinked polymer.



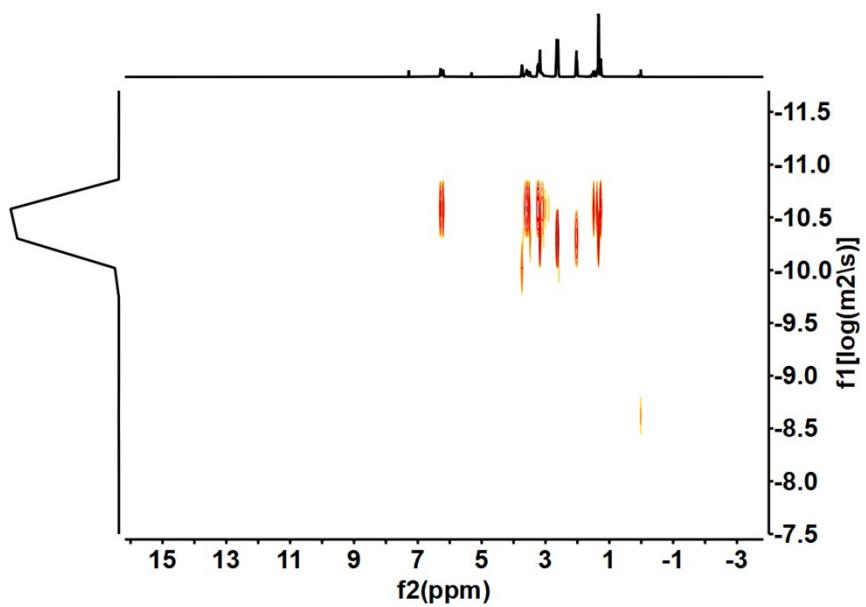
**Figure S15.** DSC thermogram of the polymer crosslinked by BDT.



**Figure S16.** DSC thermogram of the polymer crosslinked by TBT.

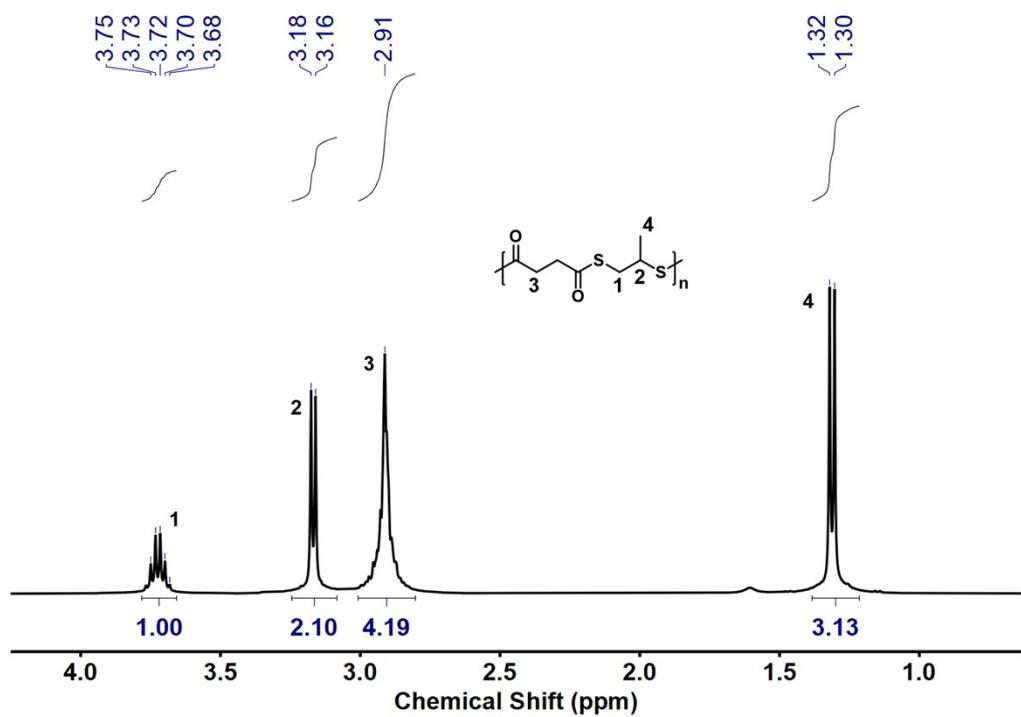


**Figure S17.** The GPC elution curves of the block polythioester.

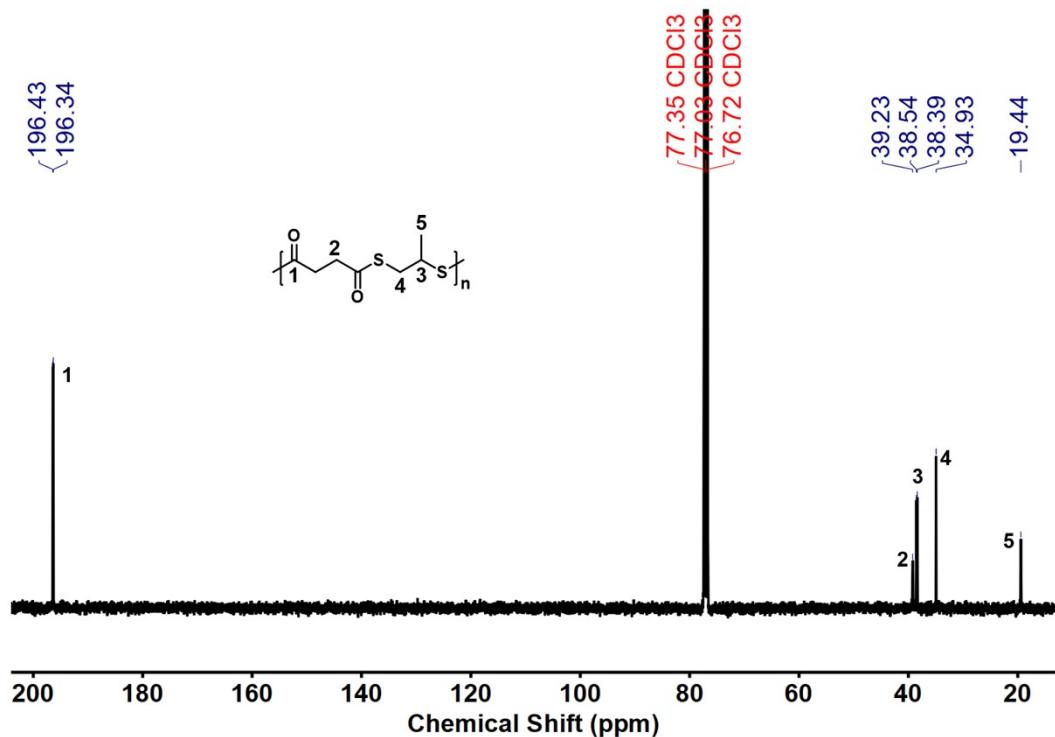


**Figure S18.** DOSY NMR spectrum of the polymer blends.

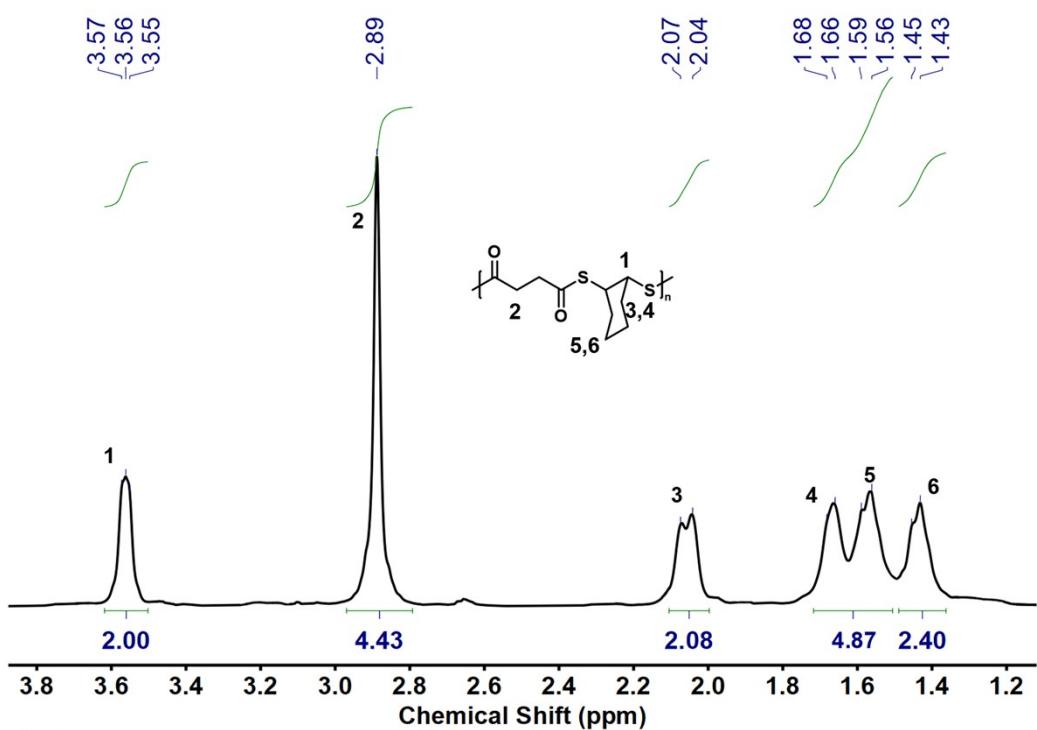
## Appendices



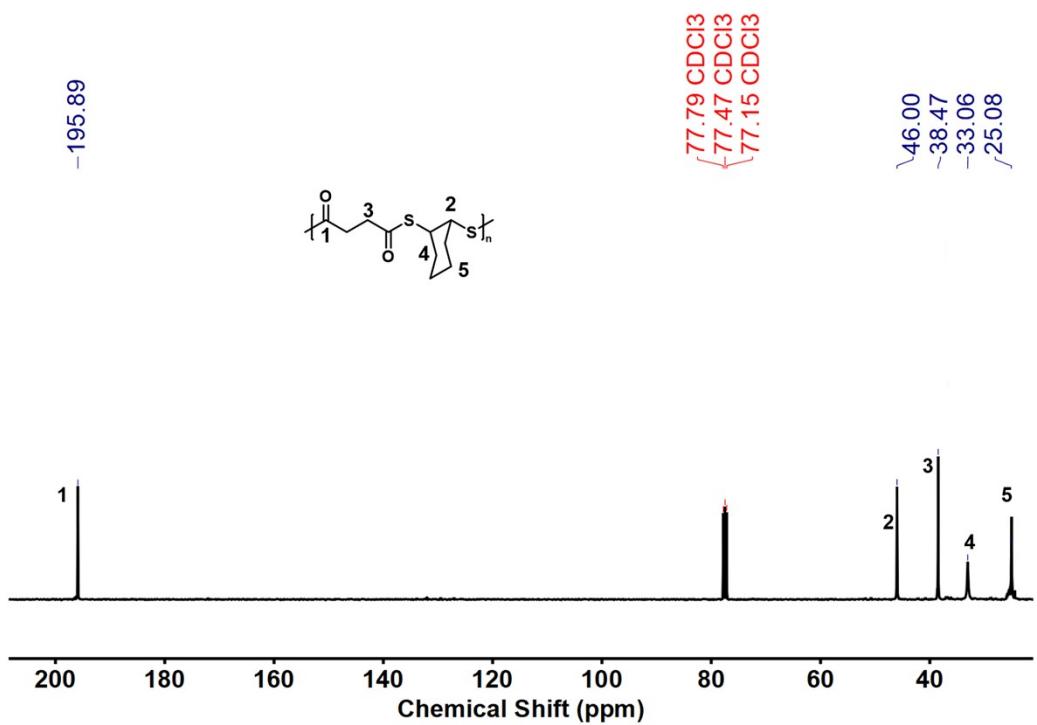
**Figure A1.**  $^1\text{H}$  NMR spectrum of poly(STAH-*alt*-PS) in  $\text{CDCl}_3$ .



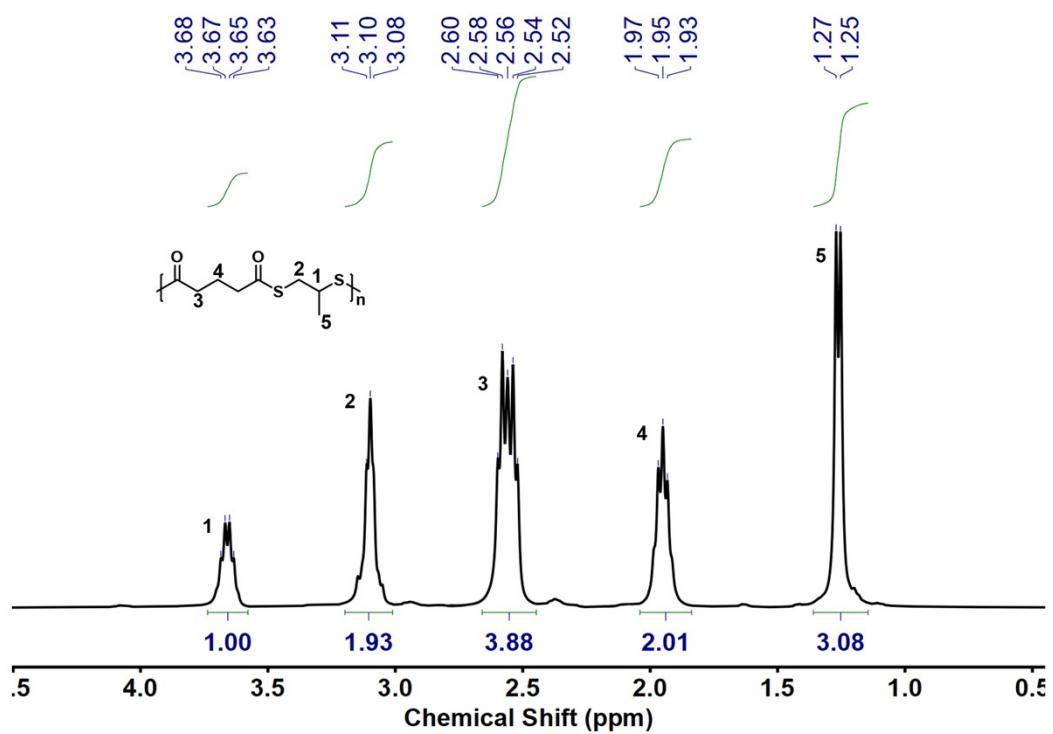
**Figure A2.**  $^{13}\text{C}$  NMR spectrum of poly(STAH-*alt*-PS) in  $\text{CDCl}_3$ .



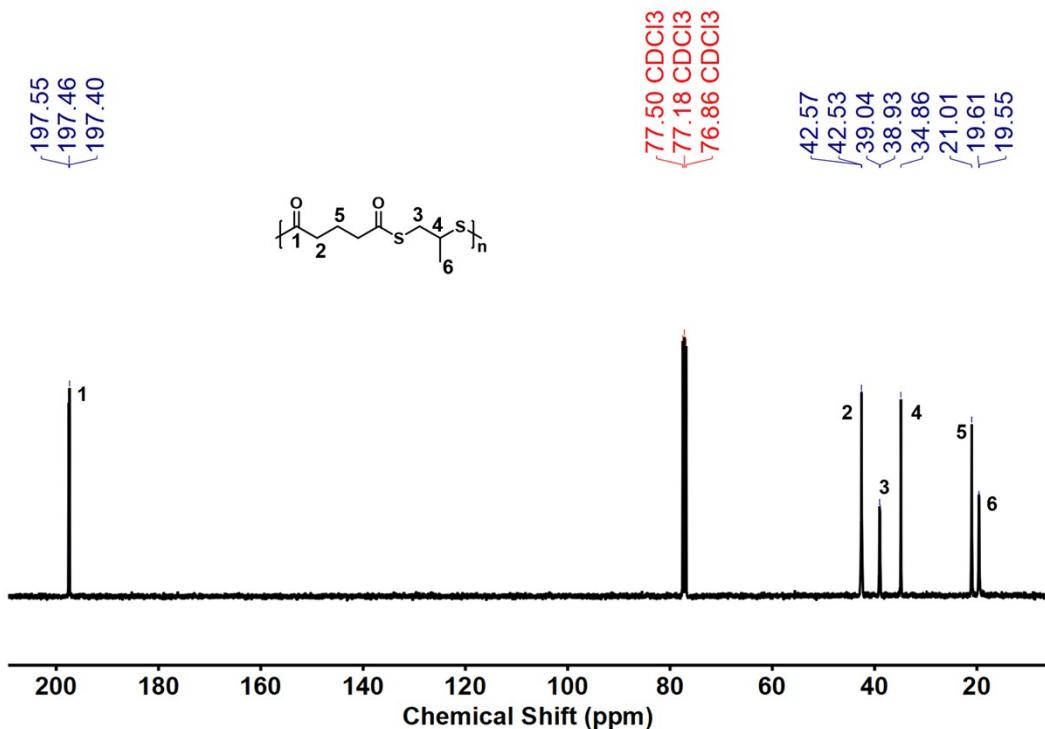
**Figure A3.**  $^1\text{H}$  NMR spectrum of poly(STAH-*alt*-CHS) in  $\text{CDCl}_3$ .



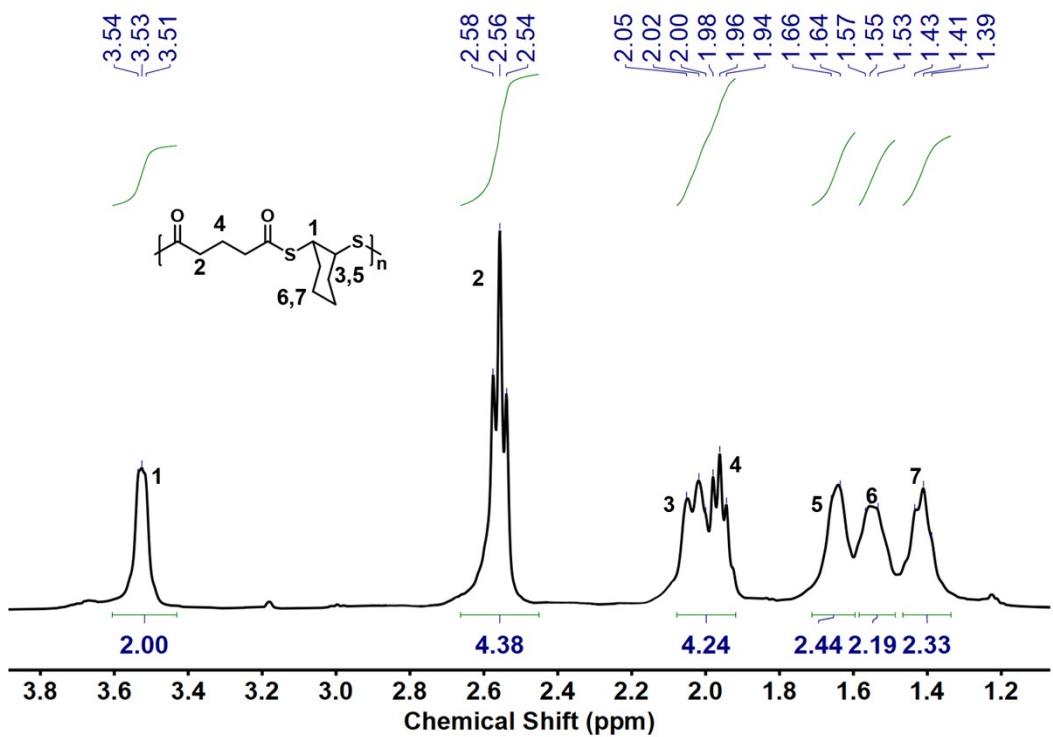
**Figure A4.**  $^{13}\text{C}$  NMR of poly(STAH-*alt*-CHS) in  $\text{CDCl}_3$ .



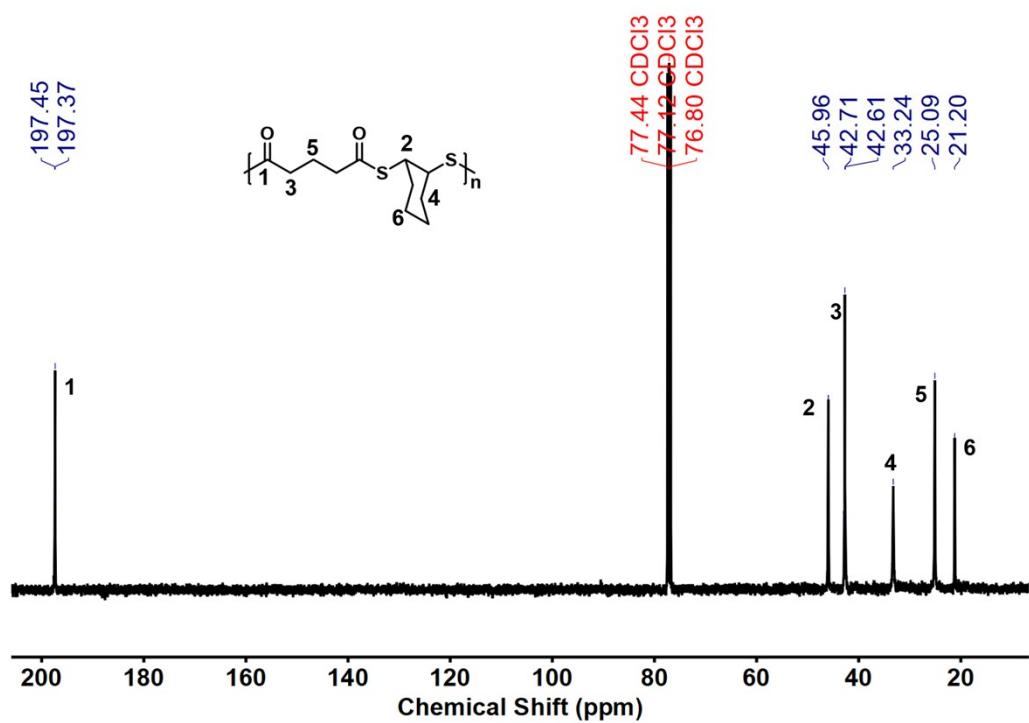
**Figure A5.** <sup>1</sup>H NMR spectrum of poly(GTAH-*alt*-PS) in CDCl<sub>3</sub>.



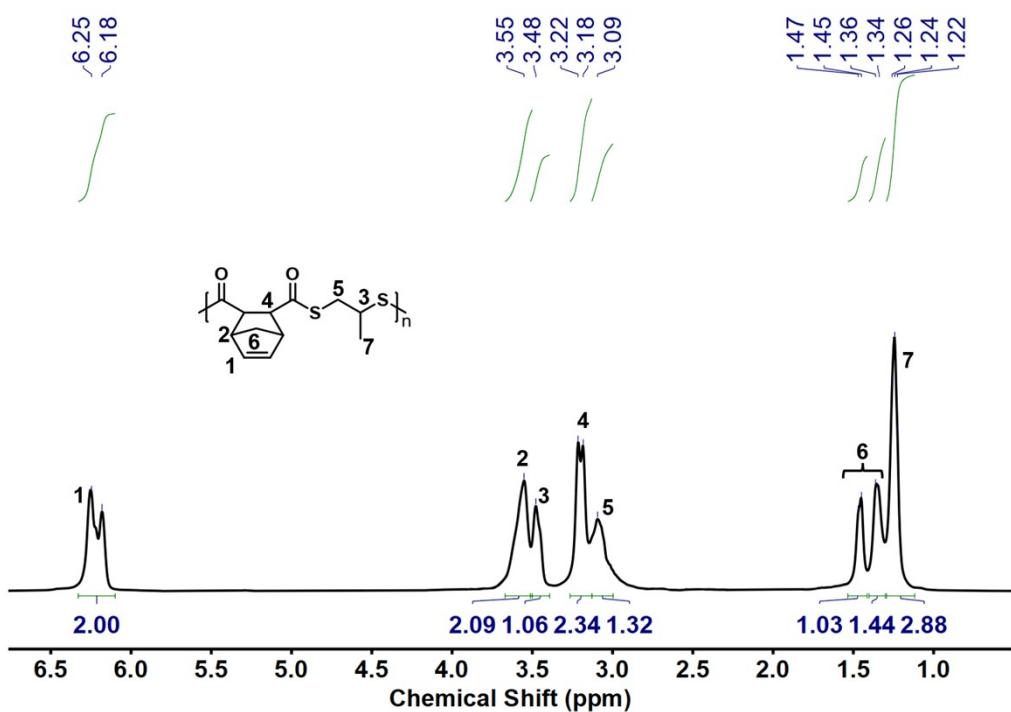
**Figure A6.** <sup>13</sup>C NMR spectrum of poly(GTAH-*alt*-PS) in CDCl<sub>3</sub>.



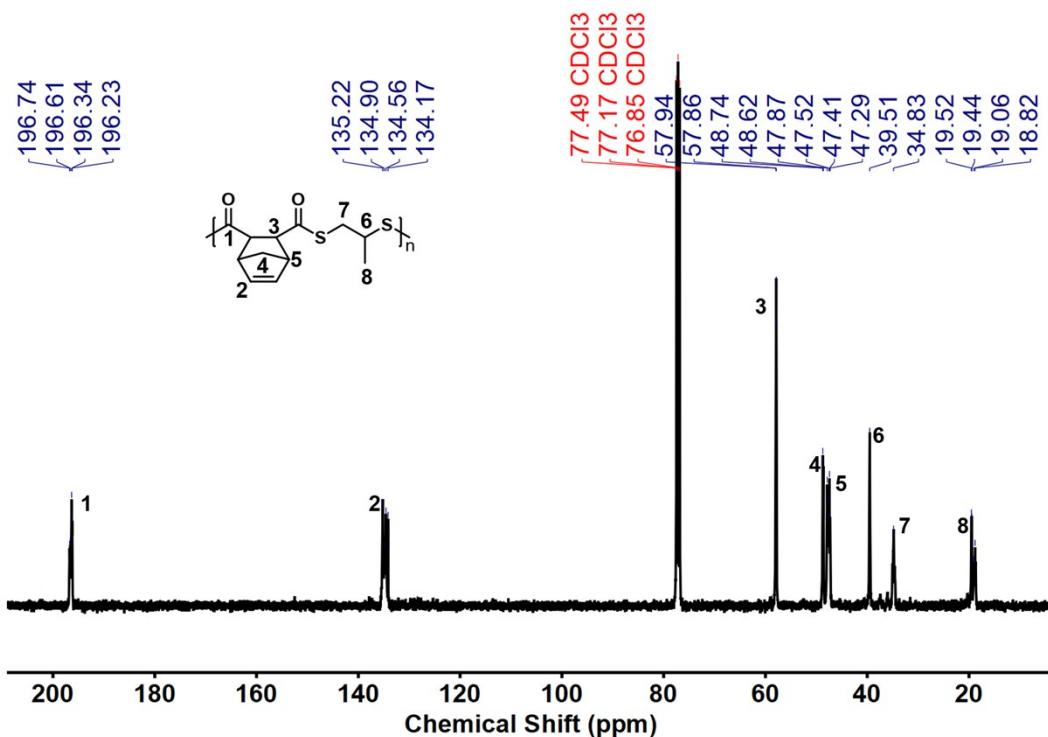
**Figure A7.**  $^1\text{H}$  NMR spectrum of poly(GTAH-*alt*-CHS) in  $\text{CDCl}_3$ .



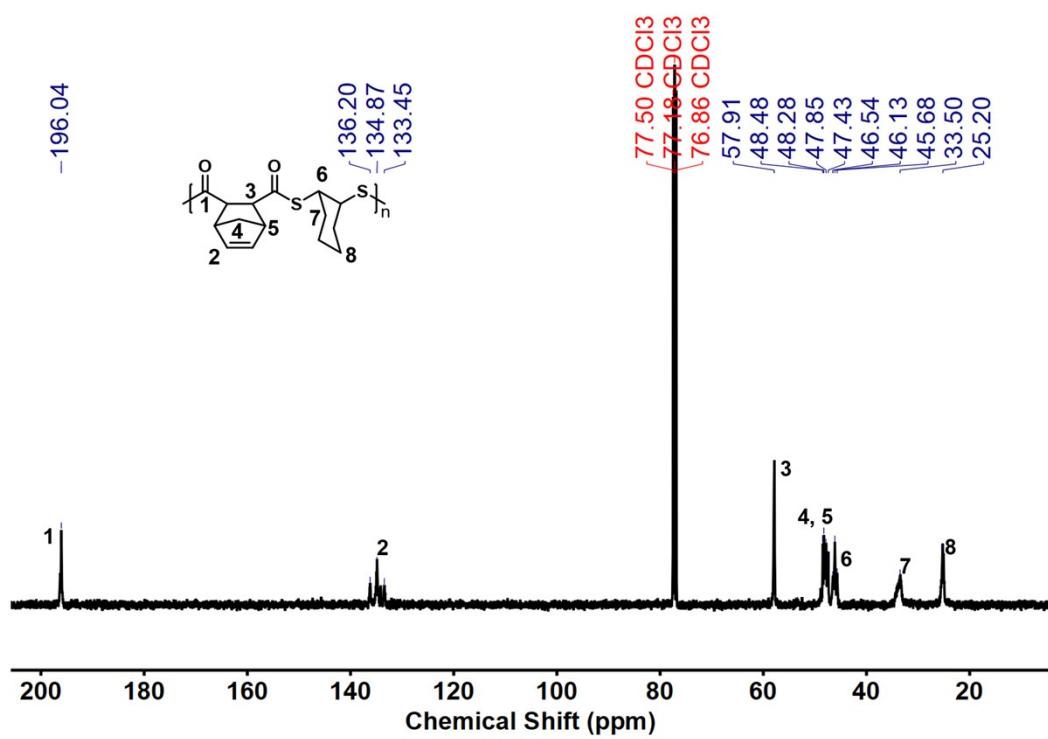
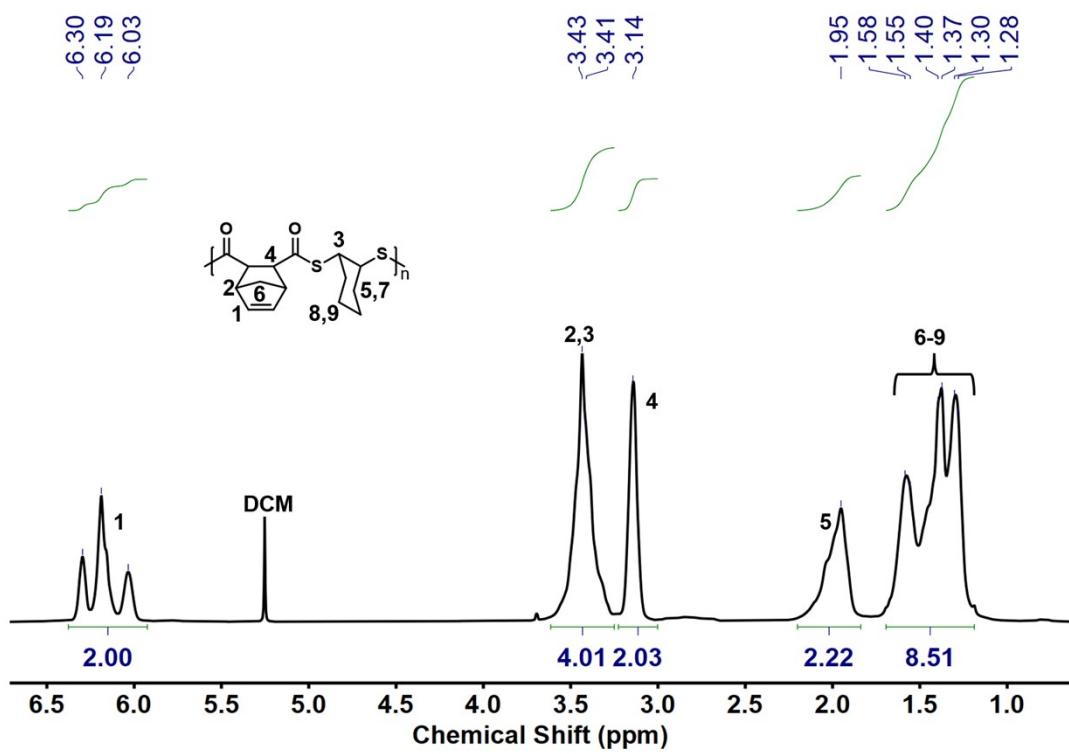
**Figure A8.**  $^{13}\text{C}$  NMR spectrum of poly(GTAH-*alt*-CHS) in  $\text{CDCl}_3$ .

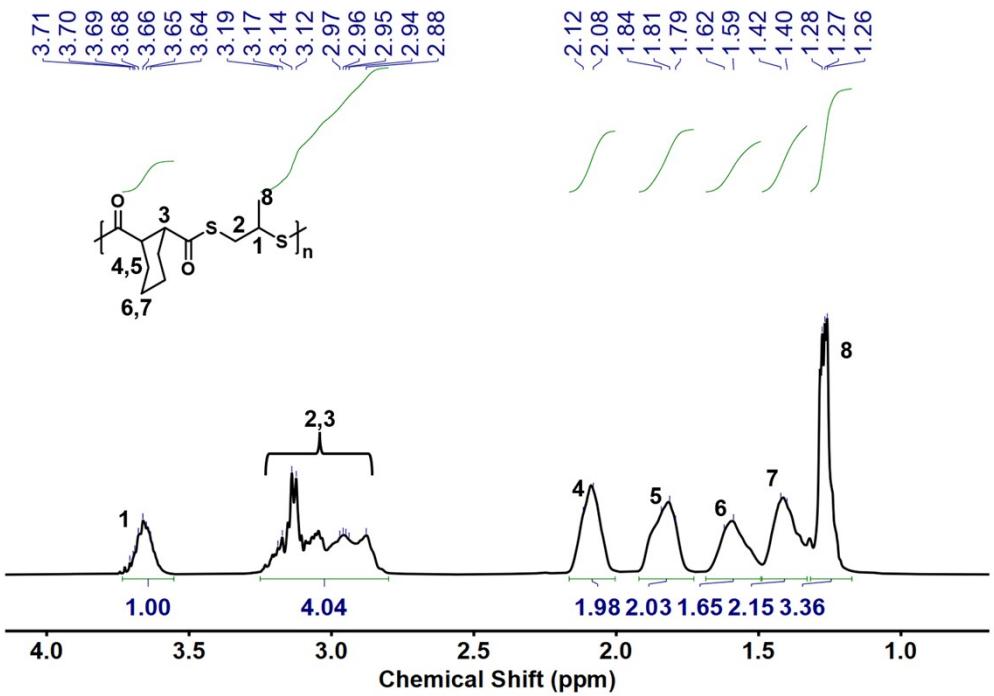


**Figure A9.** <sup>1</sup>H NMR spectrum of poly(CTAH-*alt*-PS) in CDCl<sub>3</sub>.

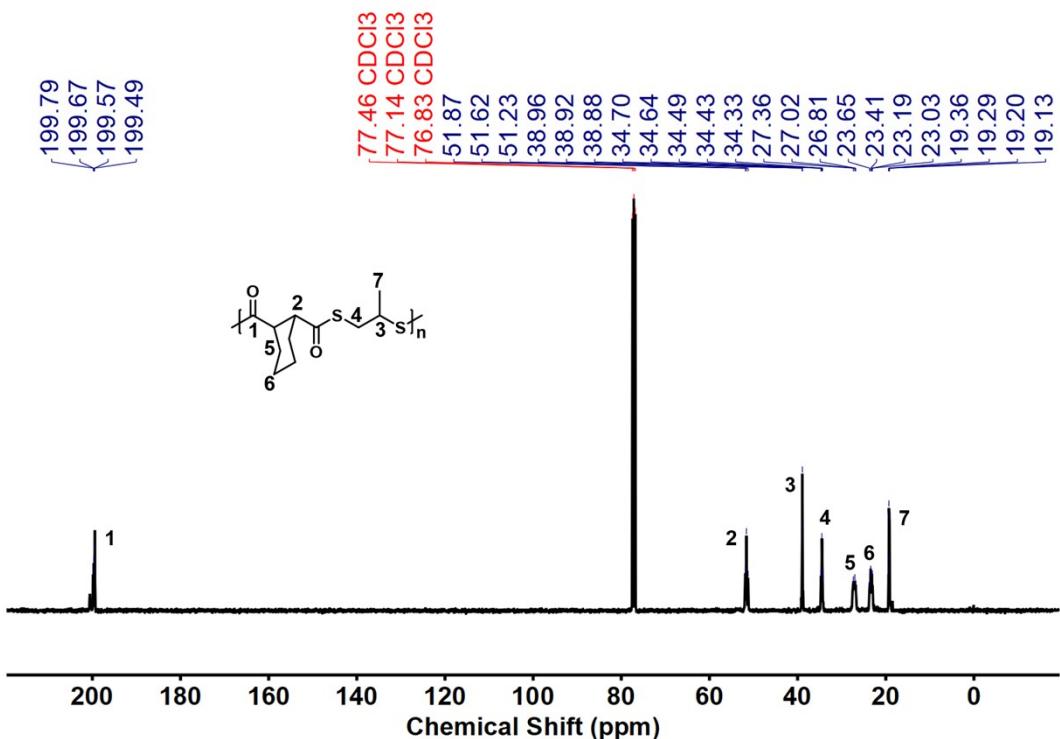


**Figure A10.** <sup>13</sup>C NMR spectrum of poly(CTAH-*alt*-PS) in CDCl<sub>3</sub>.

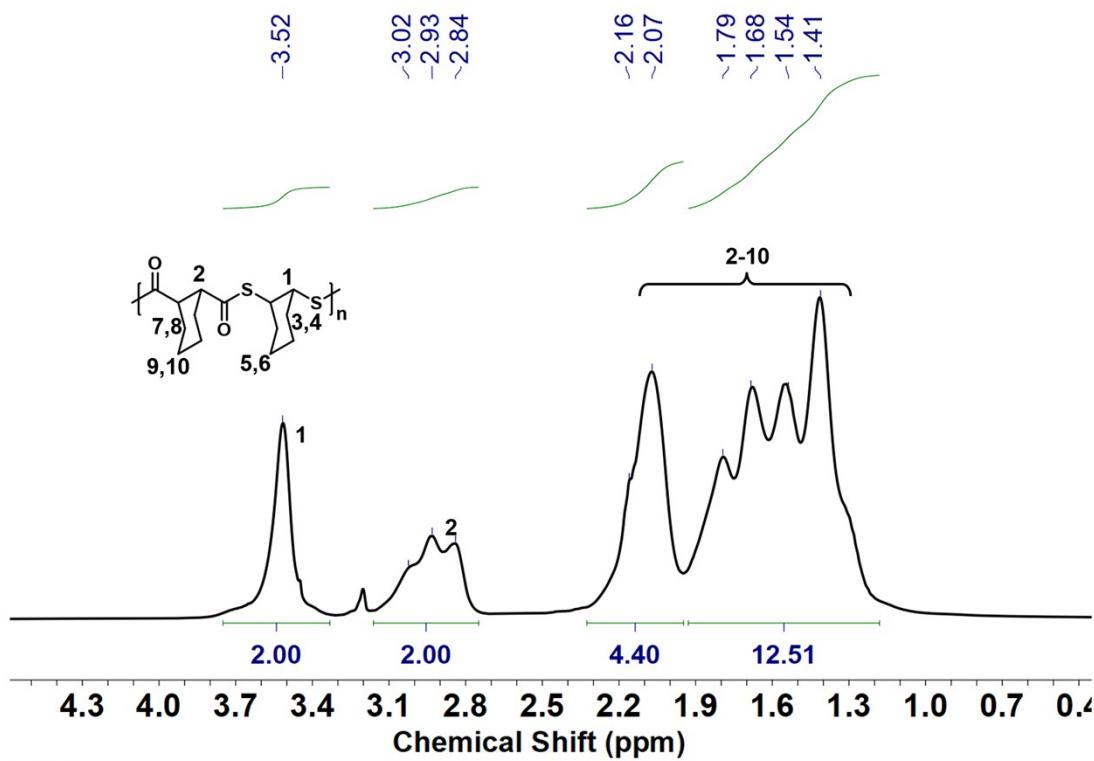




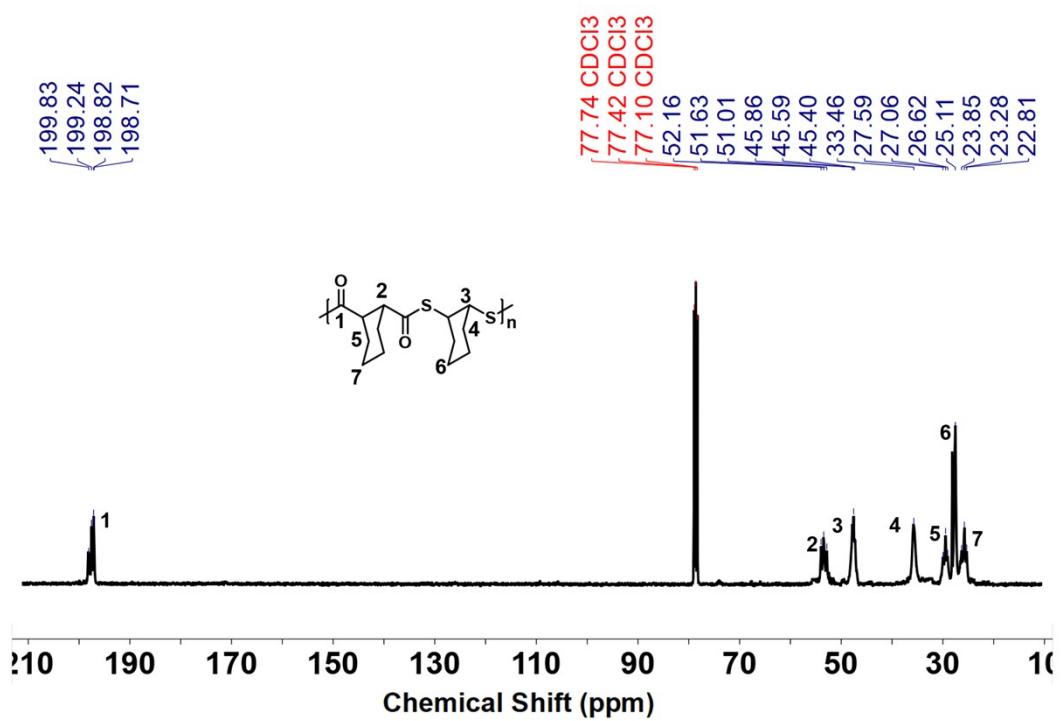
**Figure A13.** <sup>1</sup>H NMR spectrum of poly(CHTH-*alt*-PS) in CDCl<sub>3</sub>.



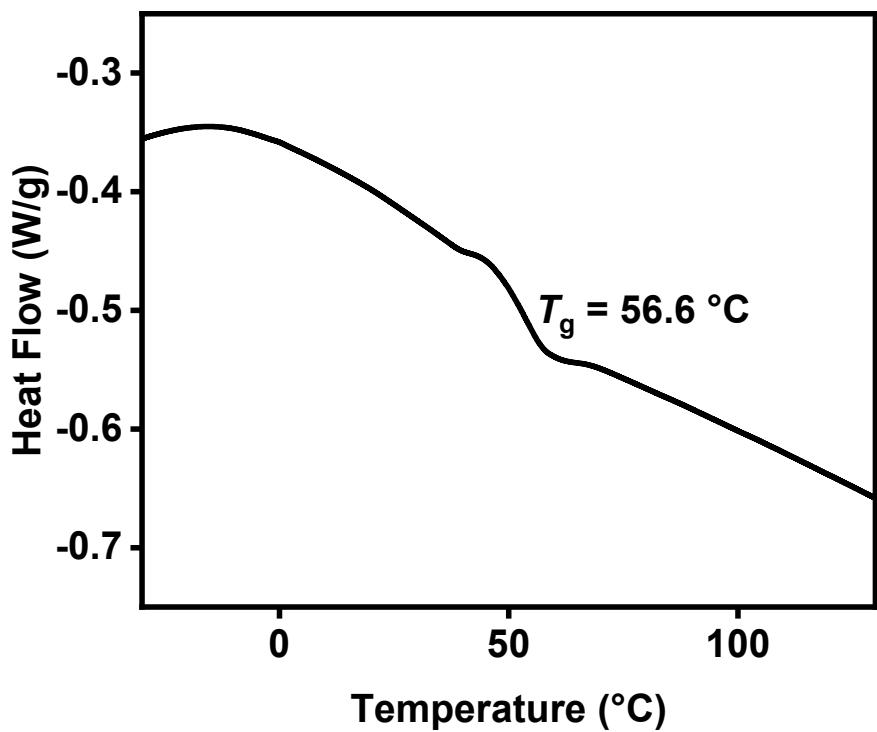
**Figure A14.** <sup>13</sup>C NMR spectrum of poly(CHTH-*alt*-PS) in CDCl<sub>3</sub>.



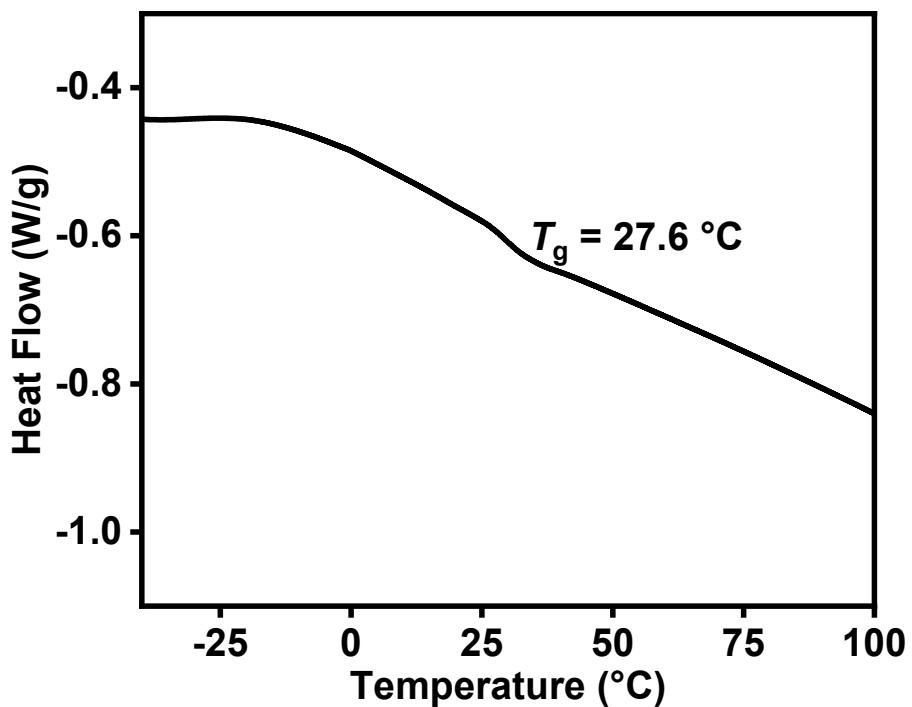
**Figure A15.** <sup>1</sup>H NMR spectrum of poly(CHTH-*alt*-CHS) in CDCl<sub>3</sub>.



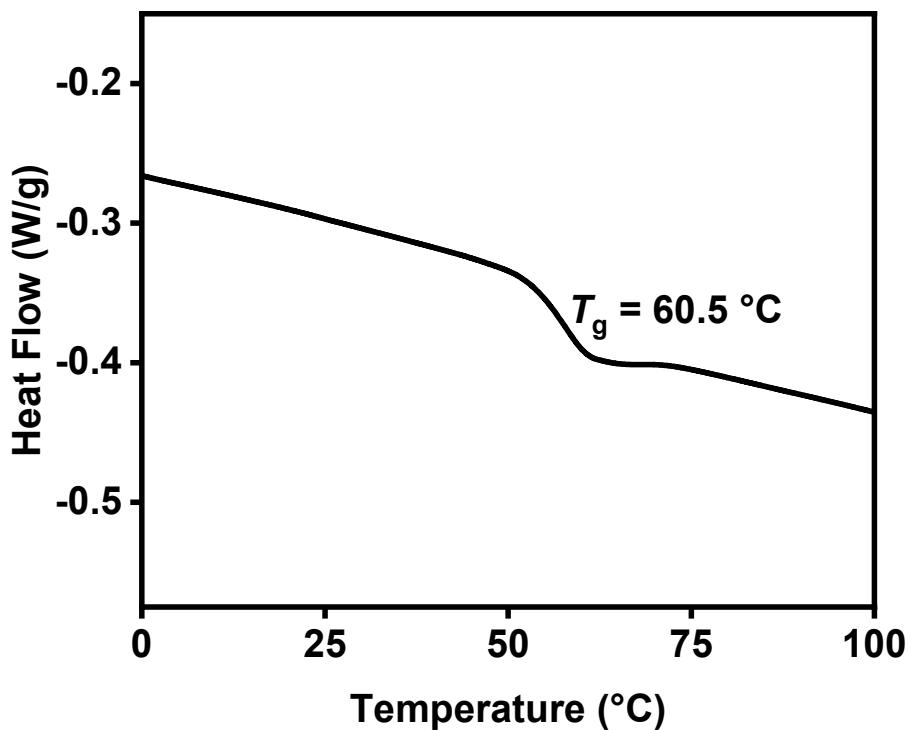
**Figure A16.** <sup>13</sup>C NMR Spectrum of poly(CHTH-*alt*-CHS) in CDCl<sub>3</sub>.



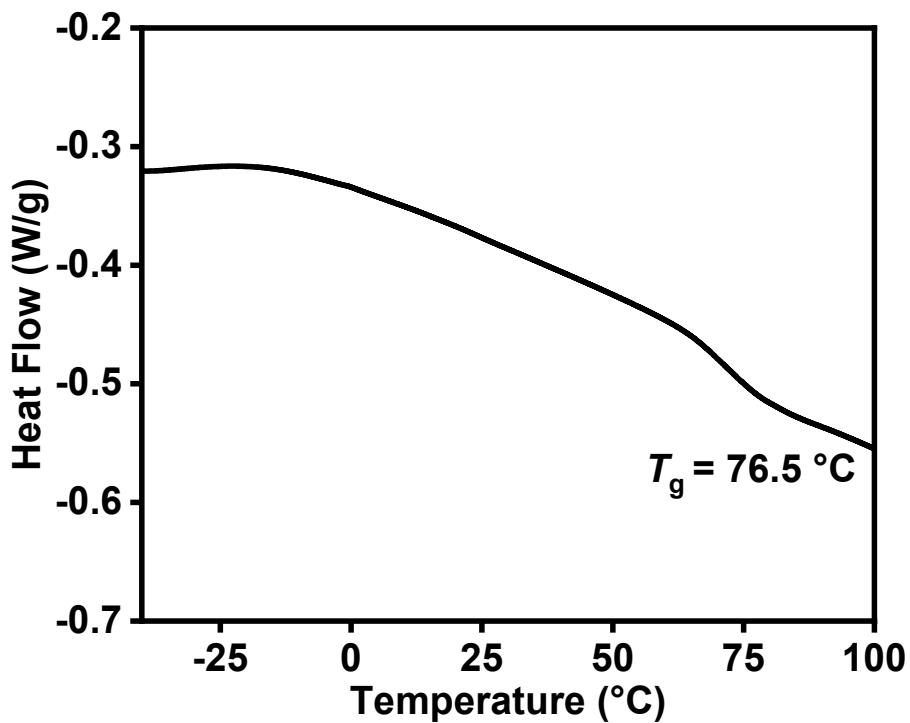
**Figure A17.** DSC thermogram of the poly(STAH-*alt*-CHS).



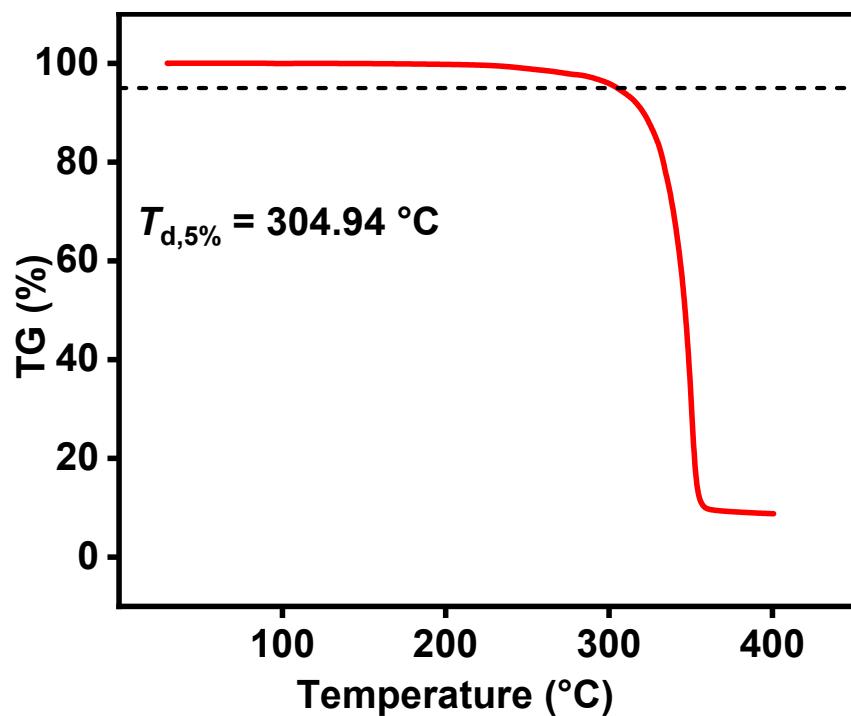
**Figure A18.** DSC thermogram of the poly(GTAH-*alt*-CHS).



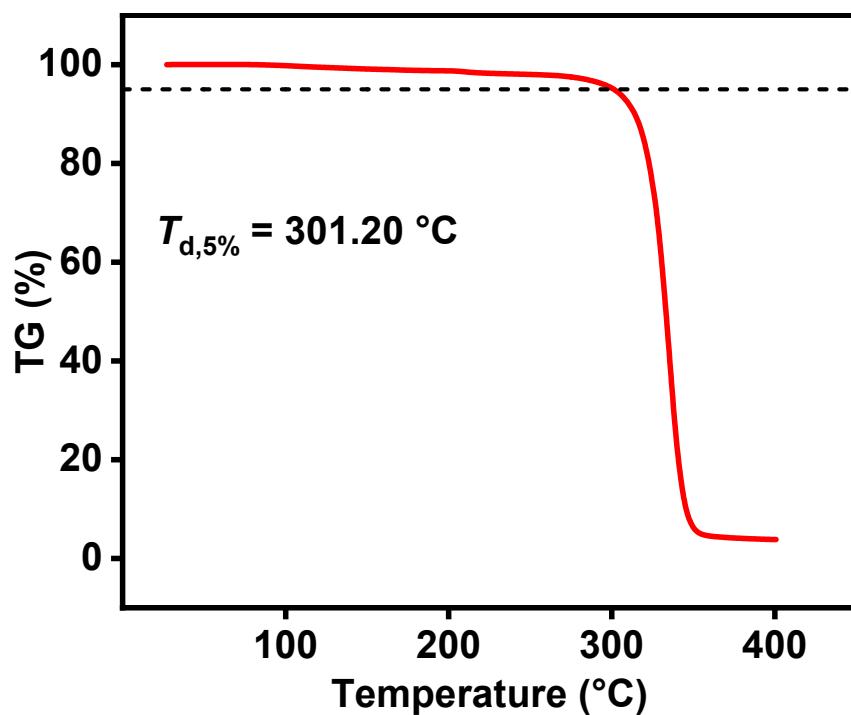
**Figure A19.** DSC thermogram of the poly(CHTH-*alt*-PS).



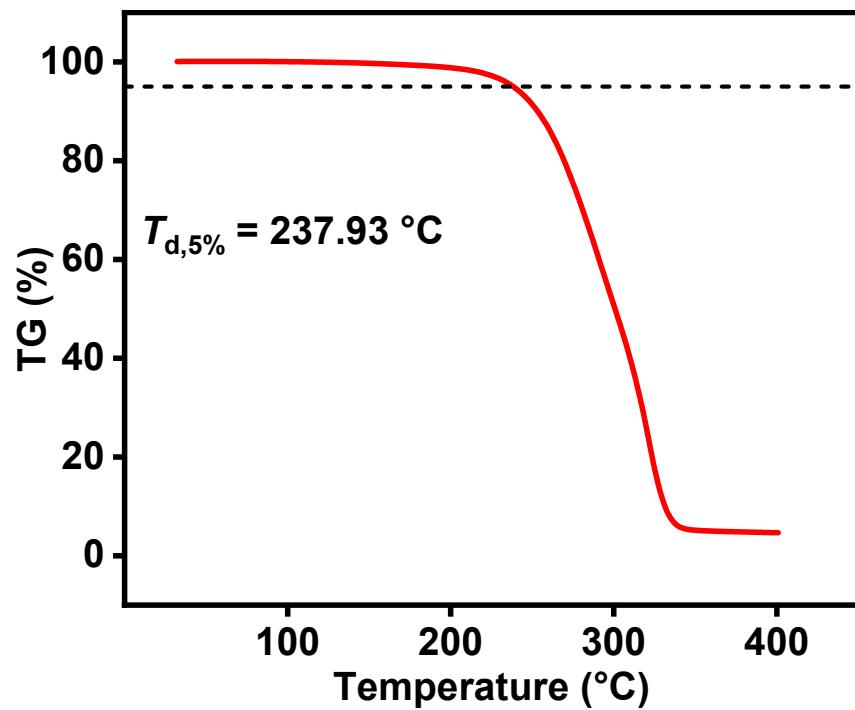
**Figure A20.** DSC thermogram of the poly(CHTH-*alt*-CHS).



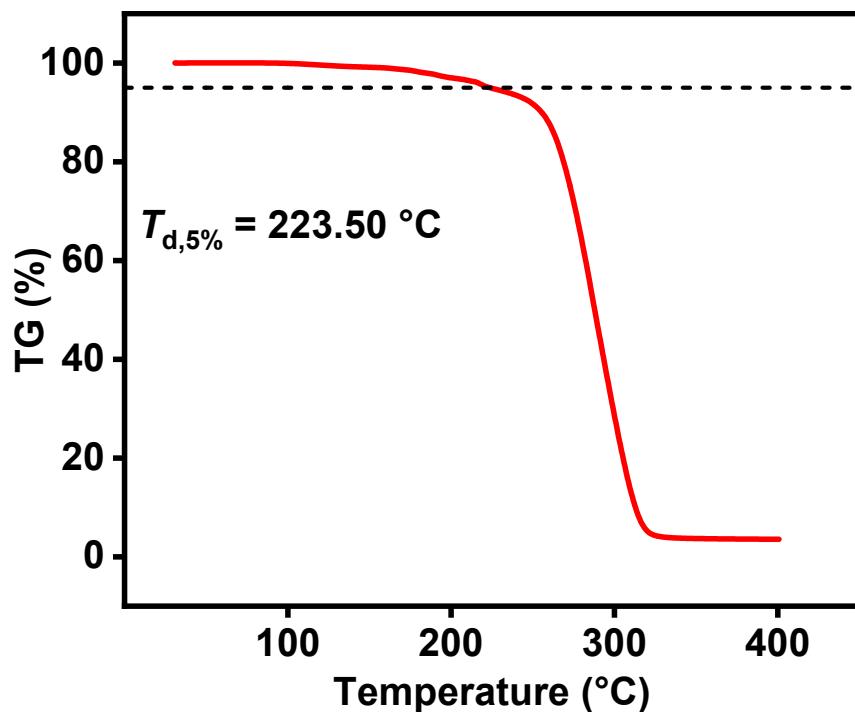
**Figure A21.** TGA curve of poly(STAH-*alt*-PS).



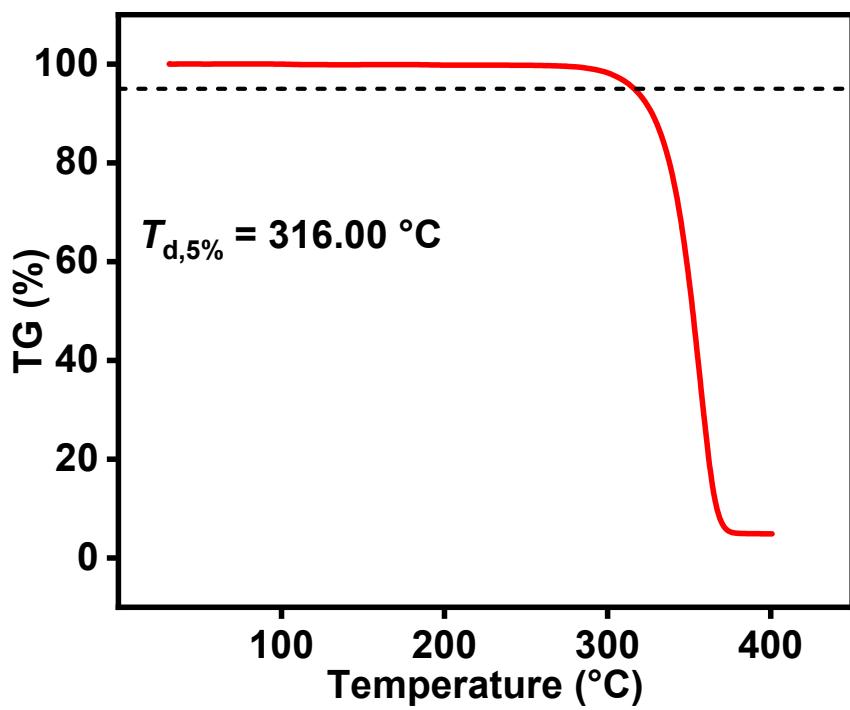
**Figure A22.** TGA curve of poly(STAH-*alt*-CHS).



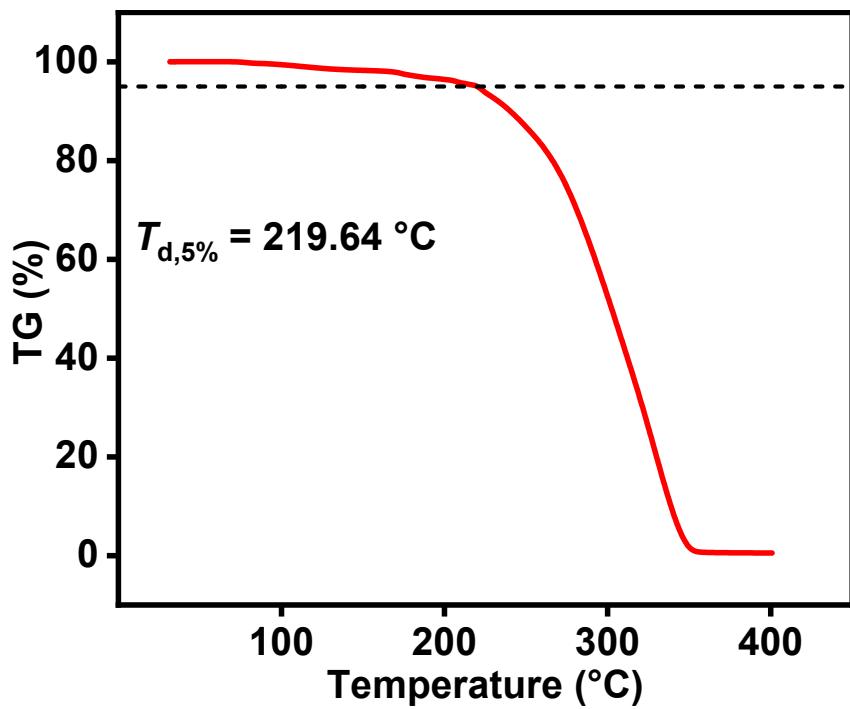
**Figure A23.** TGA curve of poly(GTAH-*alt*-PS).



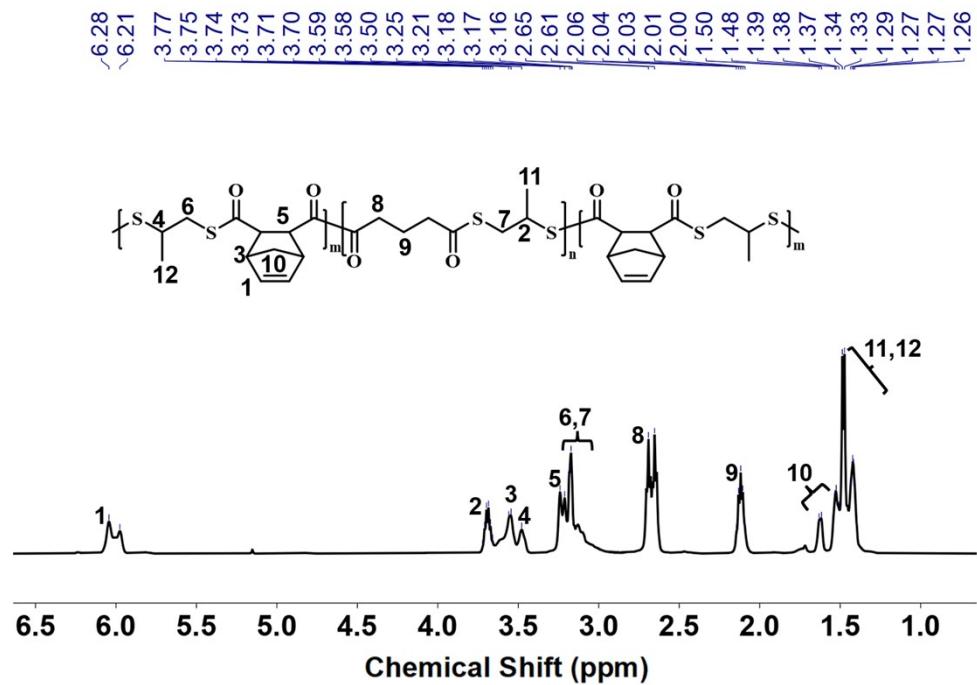
**Figure A24.** TGA curve of poly(GTAH-*alt*-CHS).



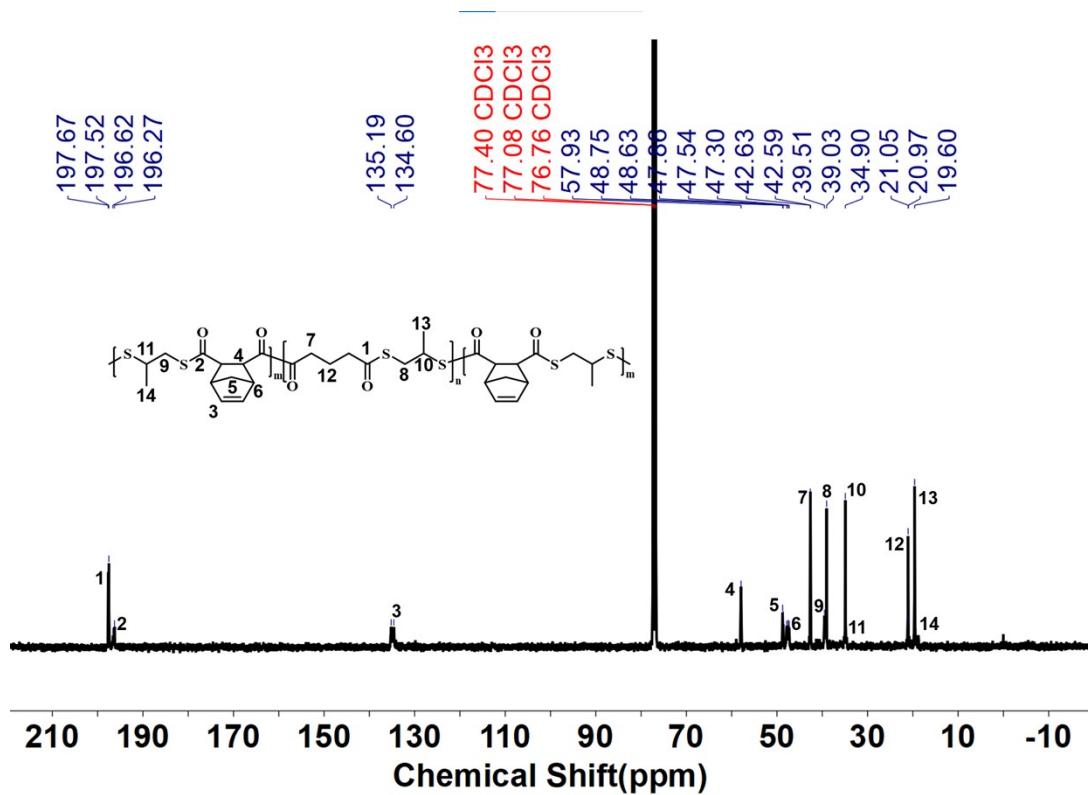
**Figure A25.** TGA curve of poly(CHTH-*alt*-PS).



**Figure A26.** TGA curve of poly(CHTH-*alt*-CHS).



**Figure A27.** <sup>1</sup>H NMR spectrum of block polythioester.



**Figure A28.** <sup>13</sup>C NMR spectrum of block polythioester.