# 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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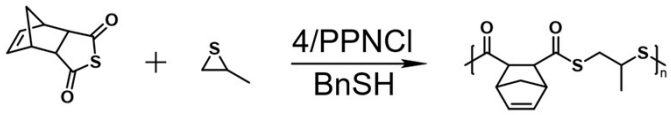
# Contents

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




| Entry[a] | CTA/Cat. | T(℃) | *t*(min) | Conv.(%)[b] | $M_{n,theo}$(kDa)[c] | $M_n$(kDa)[d] | $Đ$[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 |

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

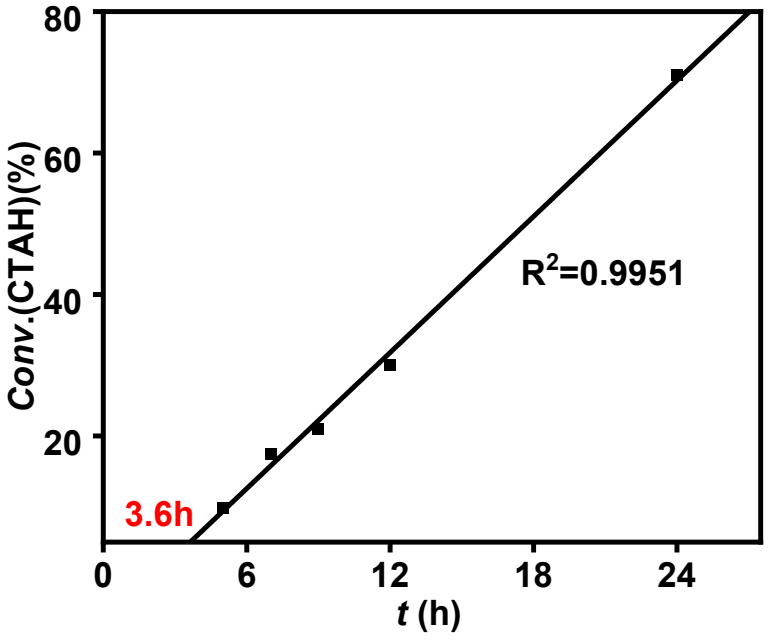



**Figure S1.** Kinetic plots of the copolymerization of CTAH and PS in toluene at 25 °C (Conditions: CTAH:PS:**4**:PPNCl = 250:250:1:1 in toluene, [PS] = 2.5 mol/L).

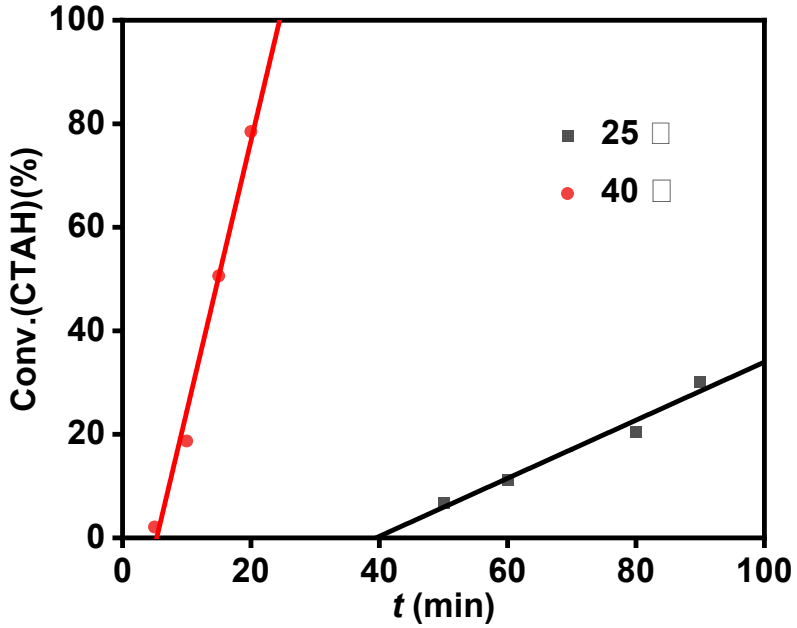



**Figure S2.** Kinetic plots of the copolymerization of CTAH and PS at 25 °C and 40 °C.

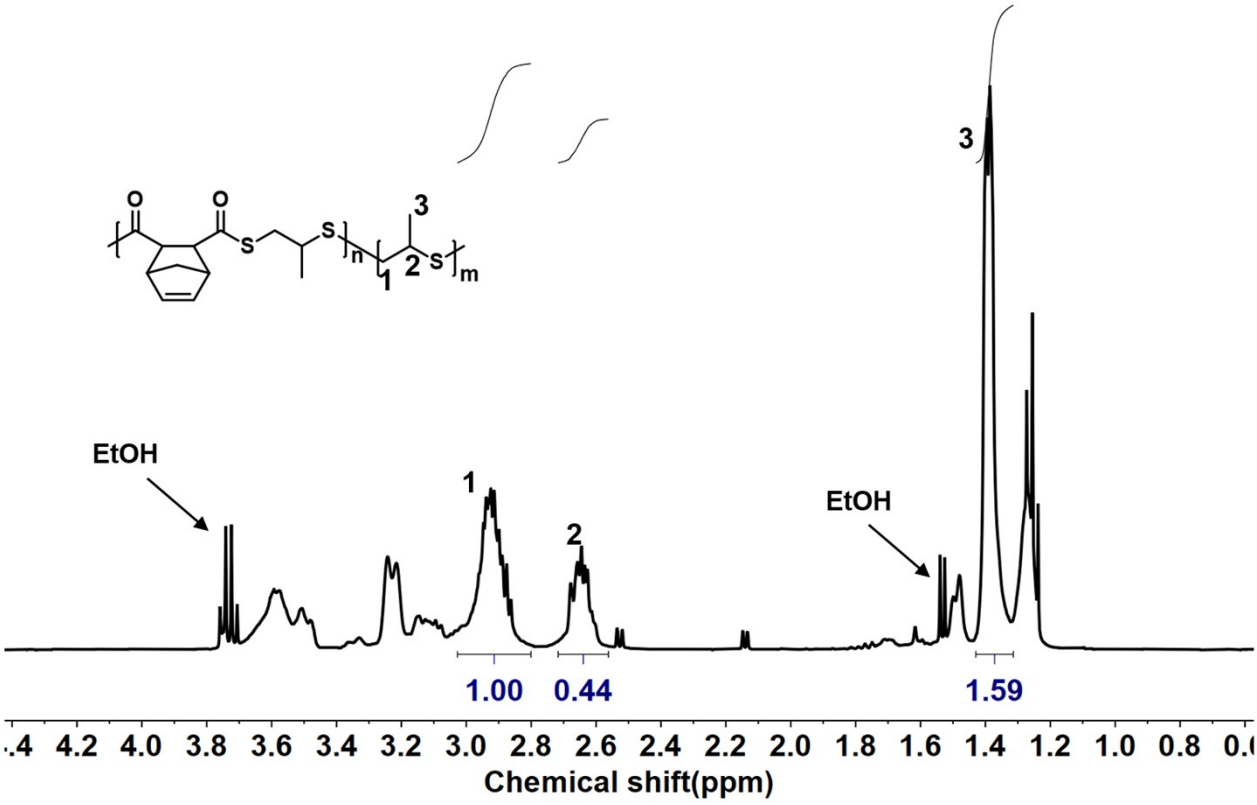



**Figure S3.** The copolymer obtained by copolymerization of CTAH and PS at 40 °C.

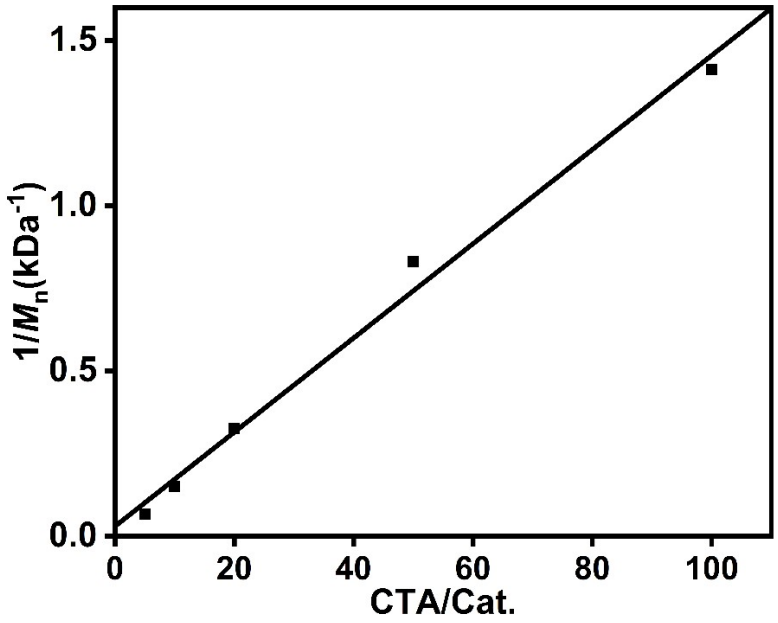



**Figure S4.** The relationship between CTA/Cat. and $M_n$.

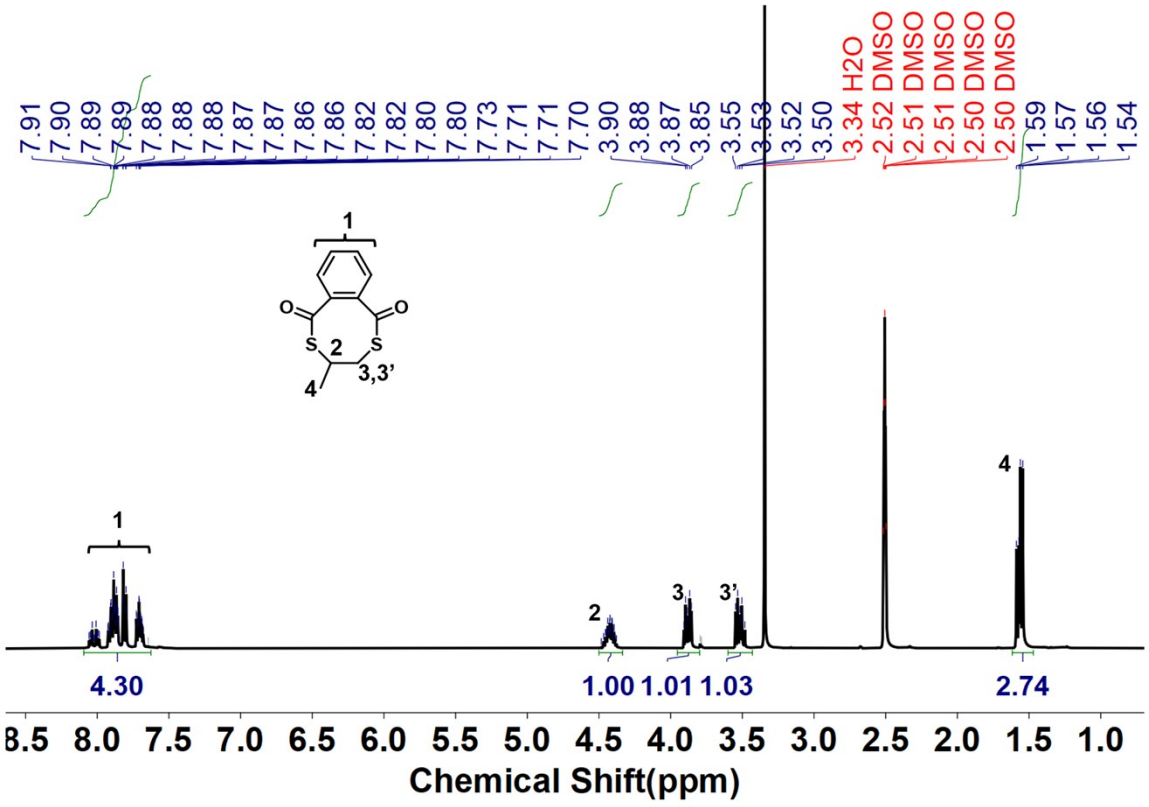



**Figure S5.** $^1$H NMR spectrum of 8-menmbered cyclic molecules in DMSO.

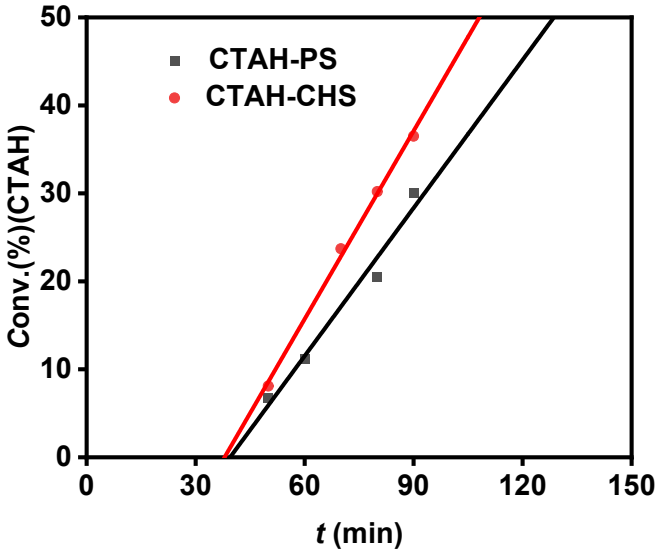



Figure S6. Kinetics of CTAH/PS copolymerisation with CTAH/CHS.

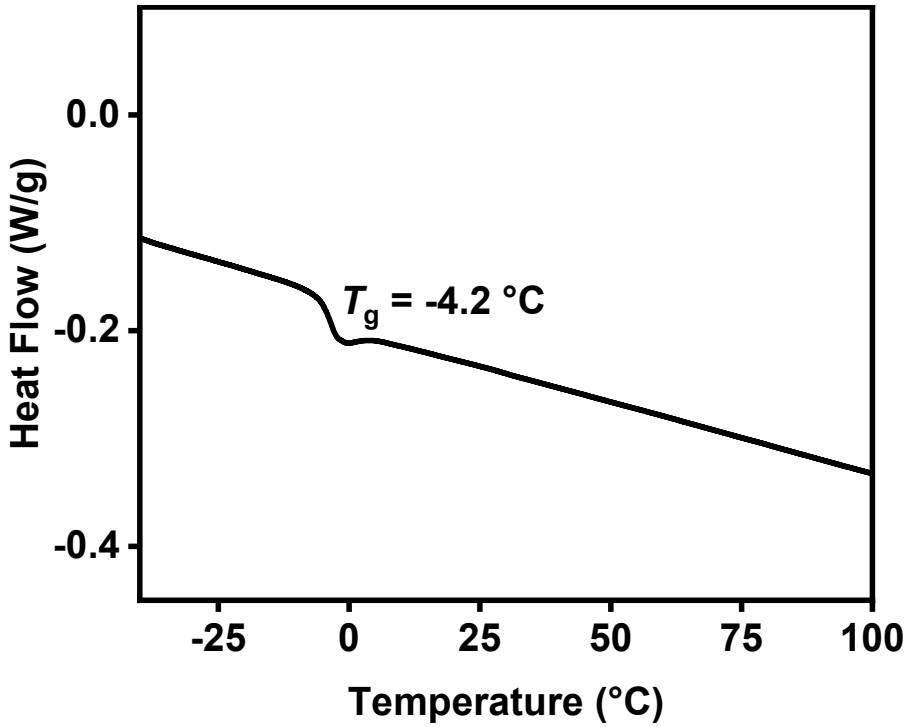



**Figure S7.** DSC thermogram of the poly(STAH-*alt*-PS).

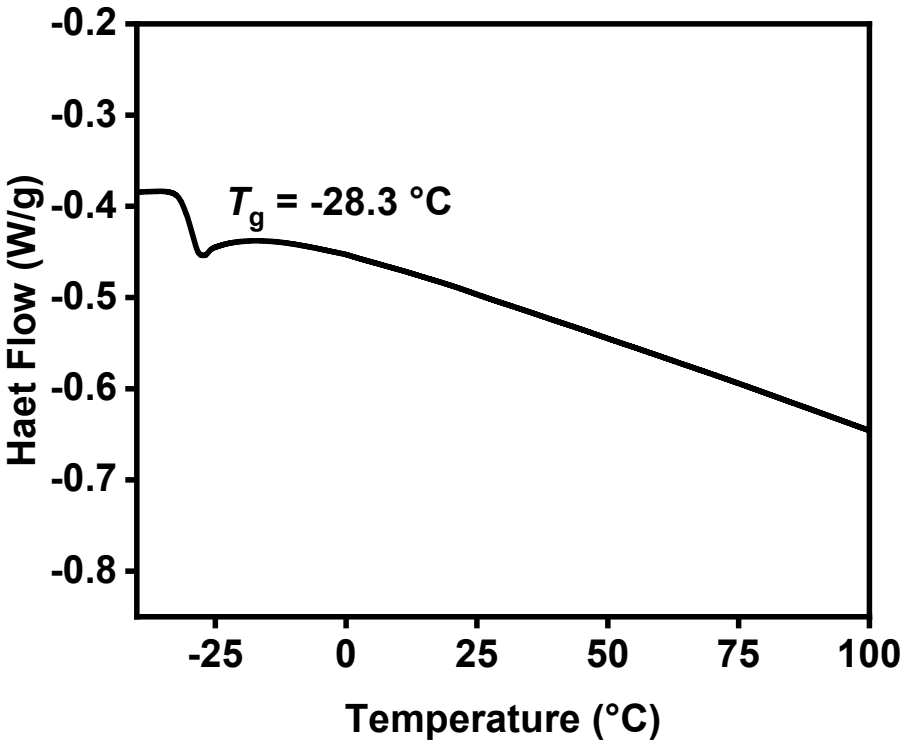



**Figure S8**. DSC thermogram of the poly(GTAH-*alt*-PS).

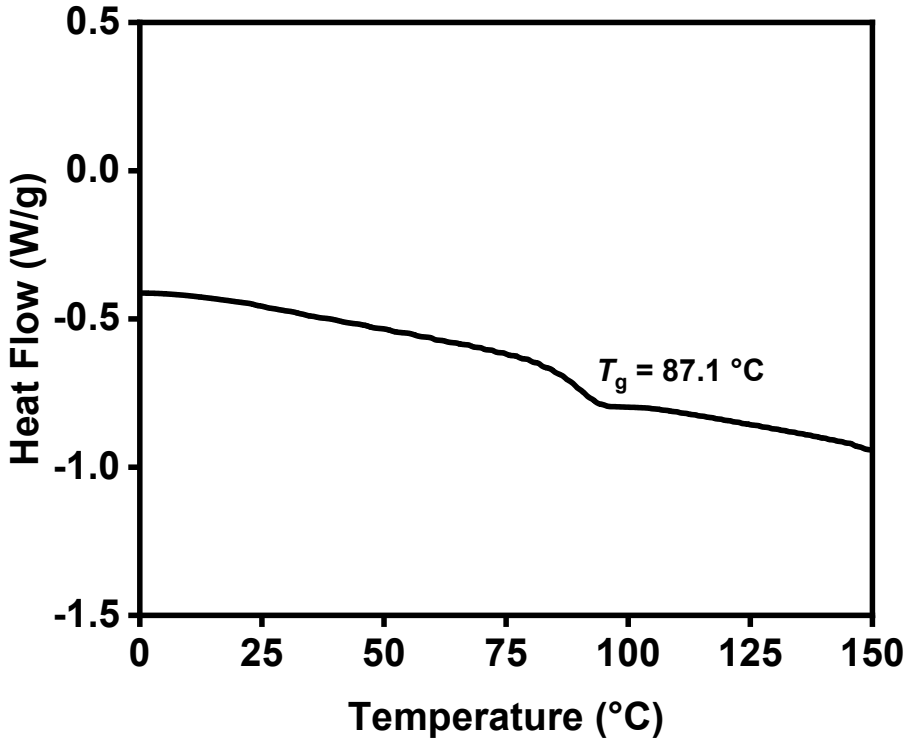



**Figure S9.** DSC thermogram of the poly(CTAH-*alt*-PS).

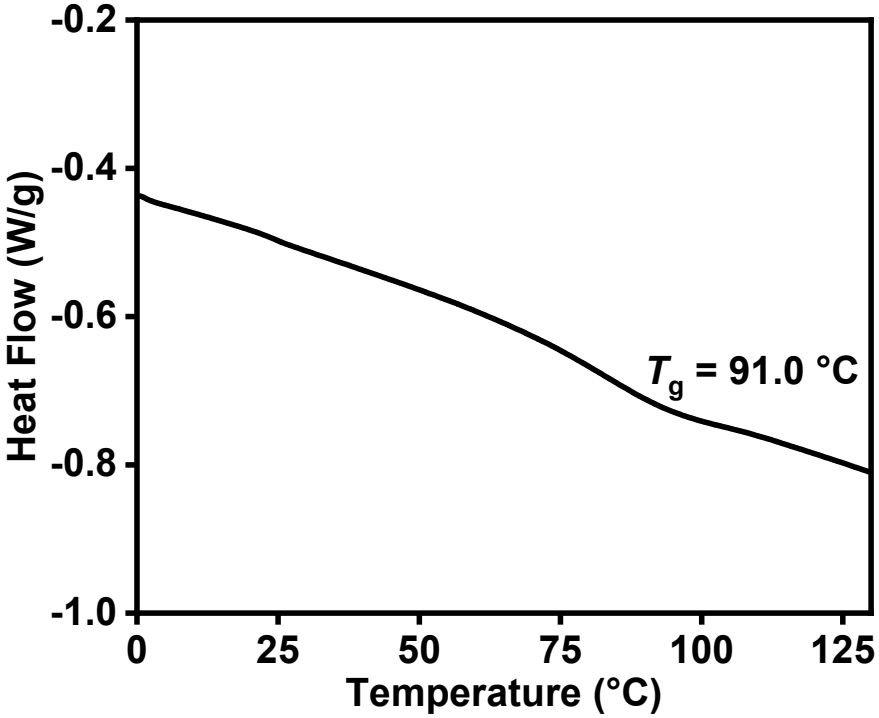



**Figure S10.** DSC thermogram of the poly(CTAH-*alt*-CHS).

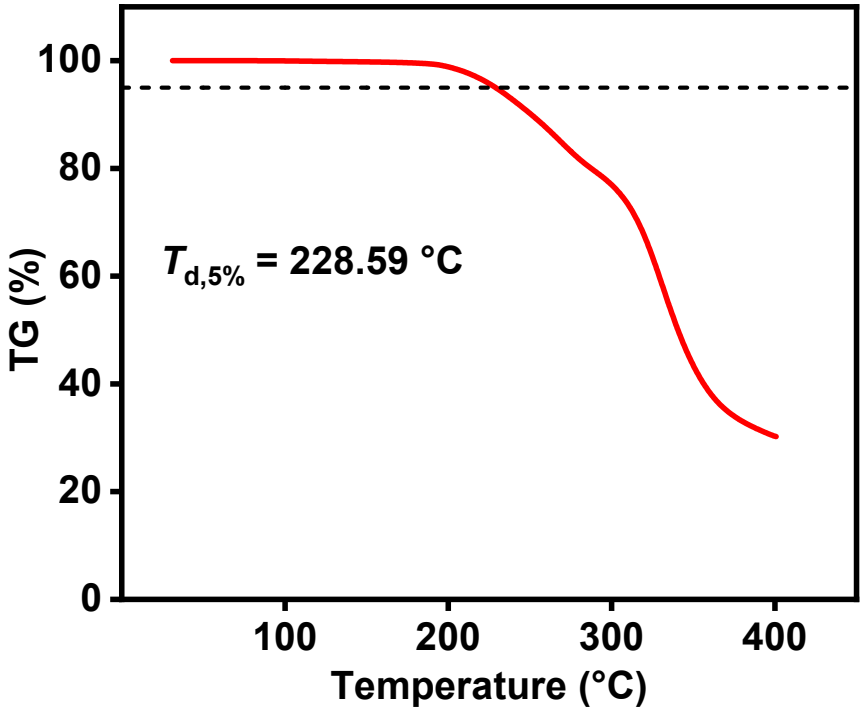



**Figure S11.** TGA curve of poly(CTAH-*alt*-PS).

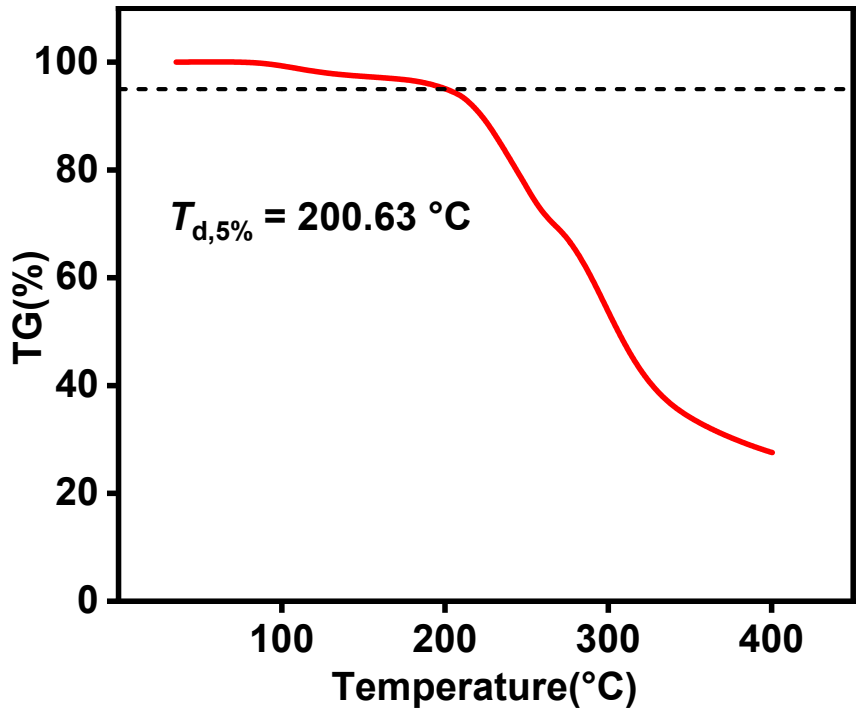



**Figure S12.** TGA curve of poly(CTAH-*alt*-CHS).

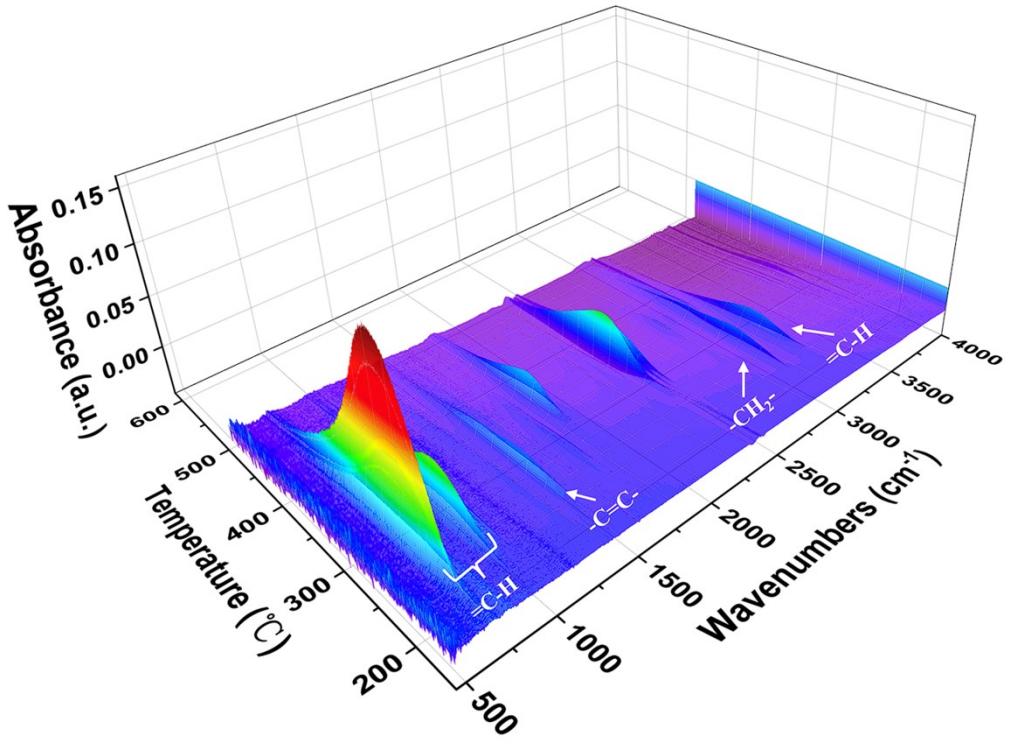



**Figure S13.** The TG-IR analysis of the poly(CTAH-alt-PS).

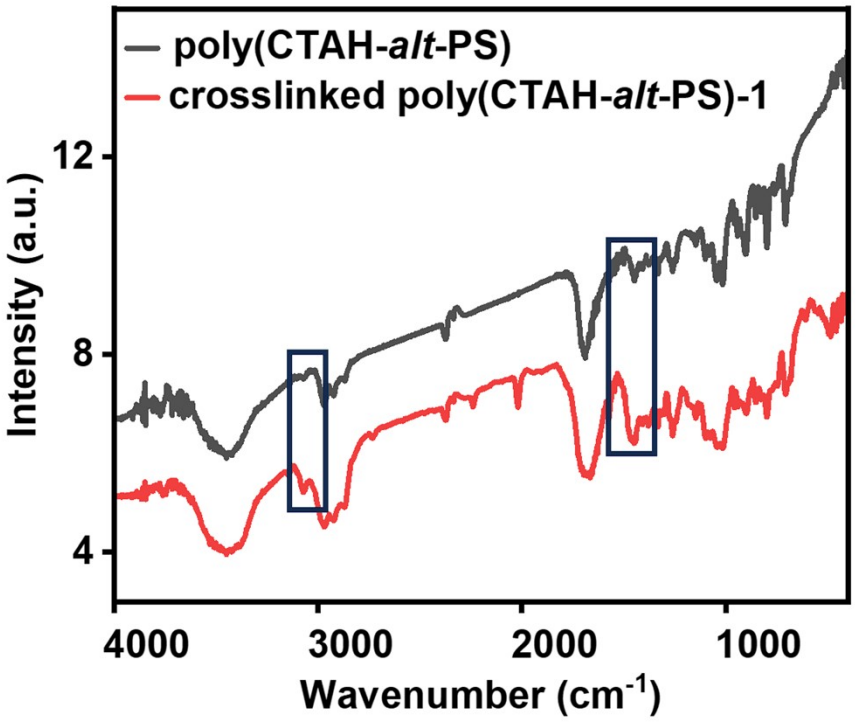



**Figure S14.** The FT-IR analysis of the poly(CTAH-*alt*-PS) and crosslinked polymer.

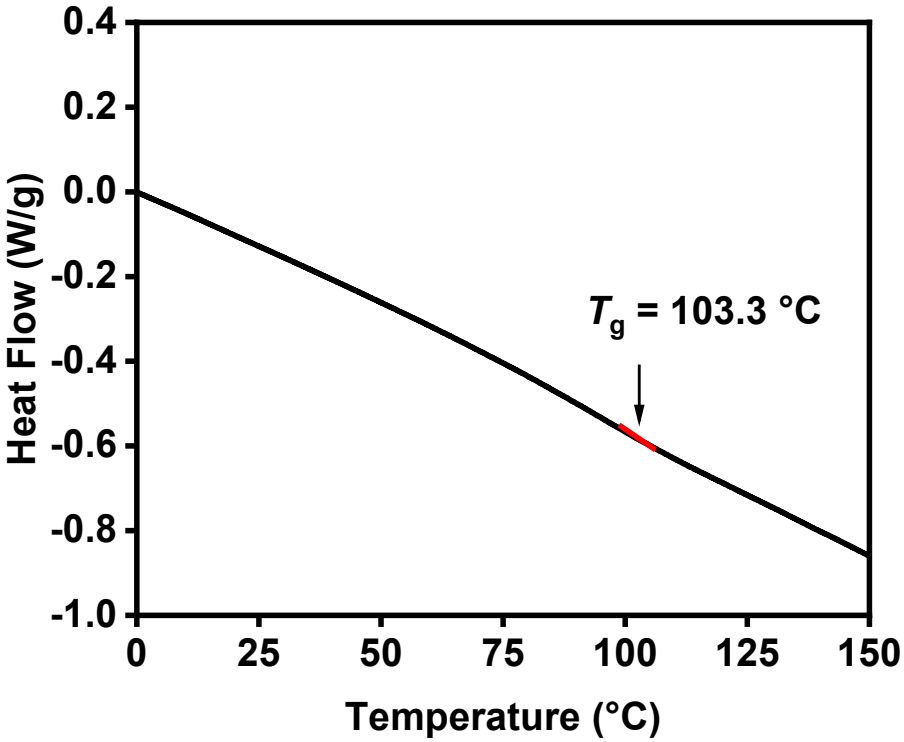



**Figure S15.** DSC thermogram of the polymer crosslinked by BDT.

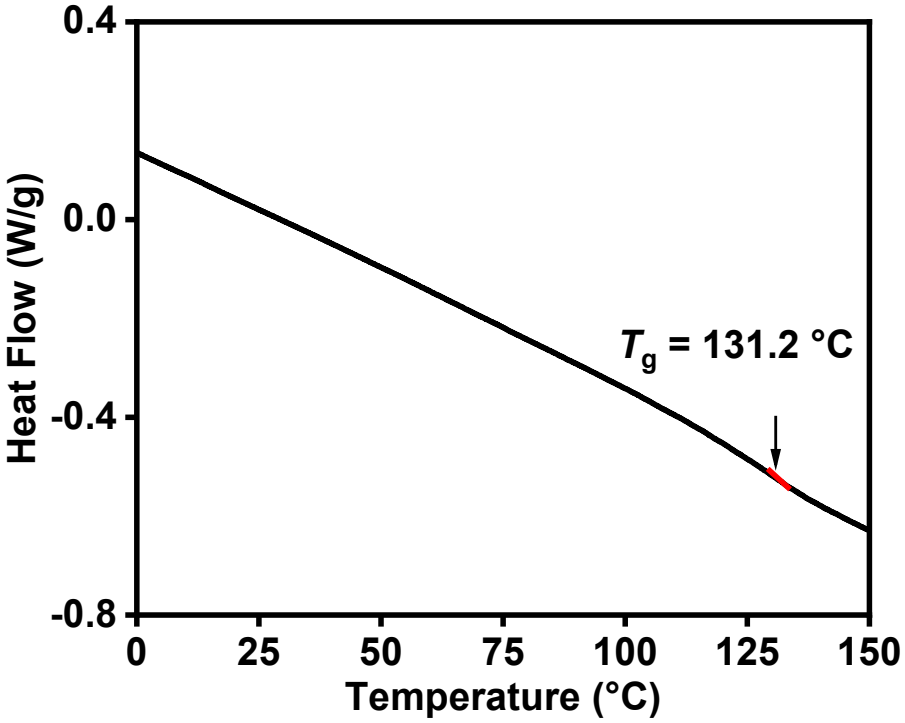



**Figure S16.** DSC thermogram of the polymer crosslinked by TBT.

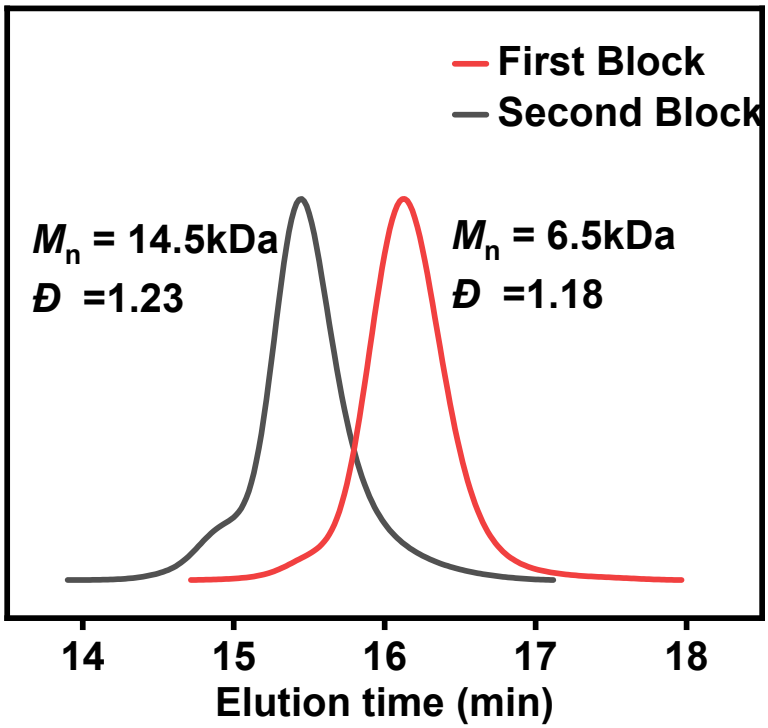



**Figure S17.** The GPC elution curves of the block polythioester.

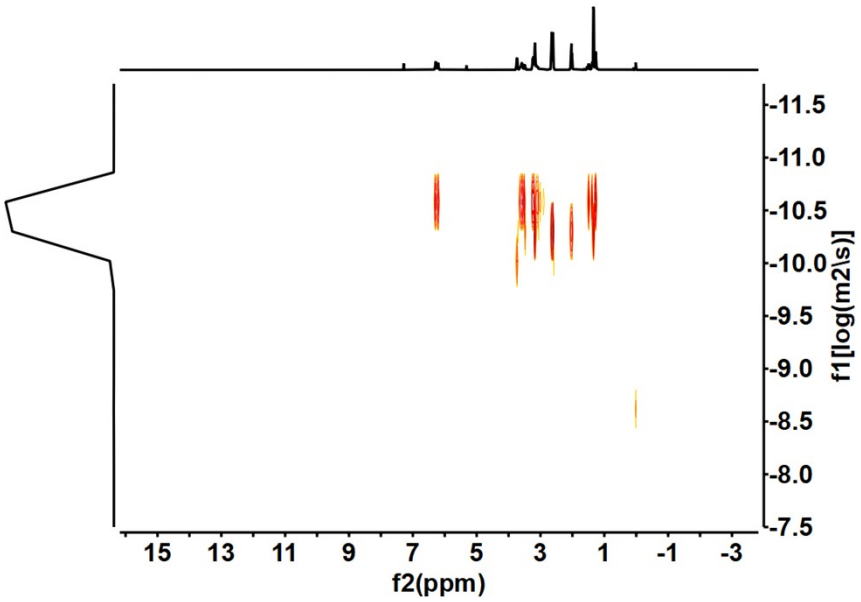



**Figure S18.** DOSY NMR spectrum of the polymer blends.

# Appendixes

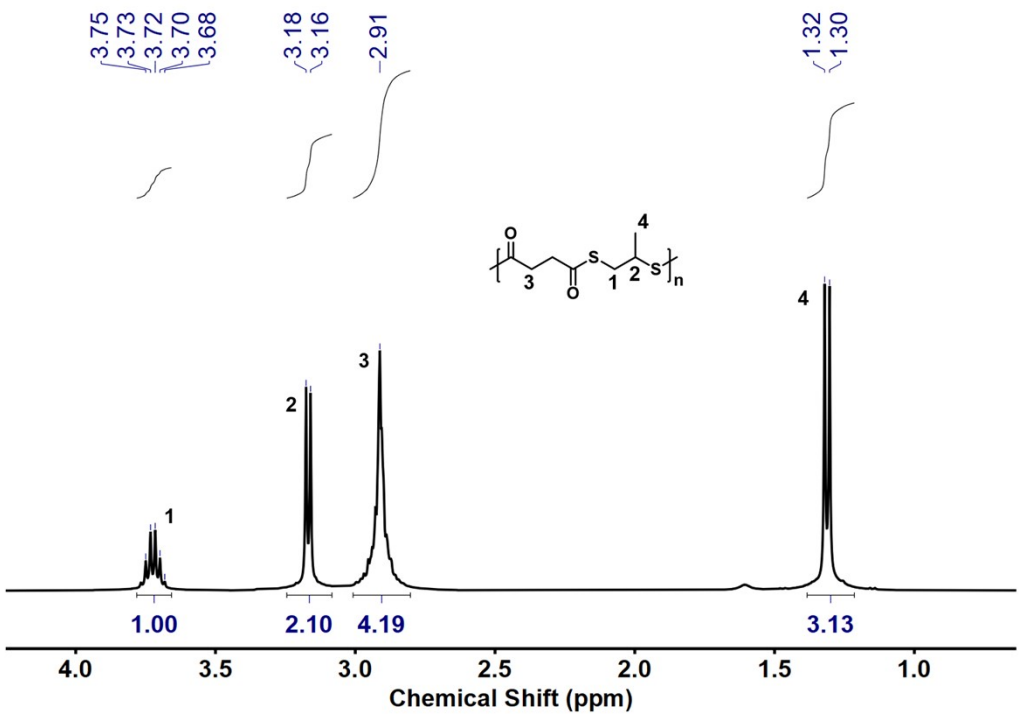



**Figure A1.** $^{1}H$ NMR spectrum of poly(STAH-*alt*-PS) in $CDCl_3$.

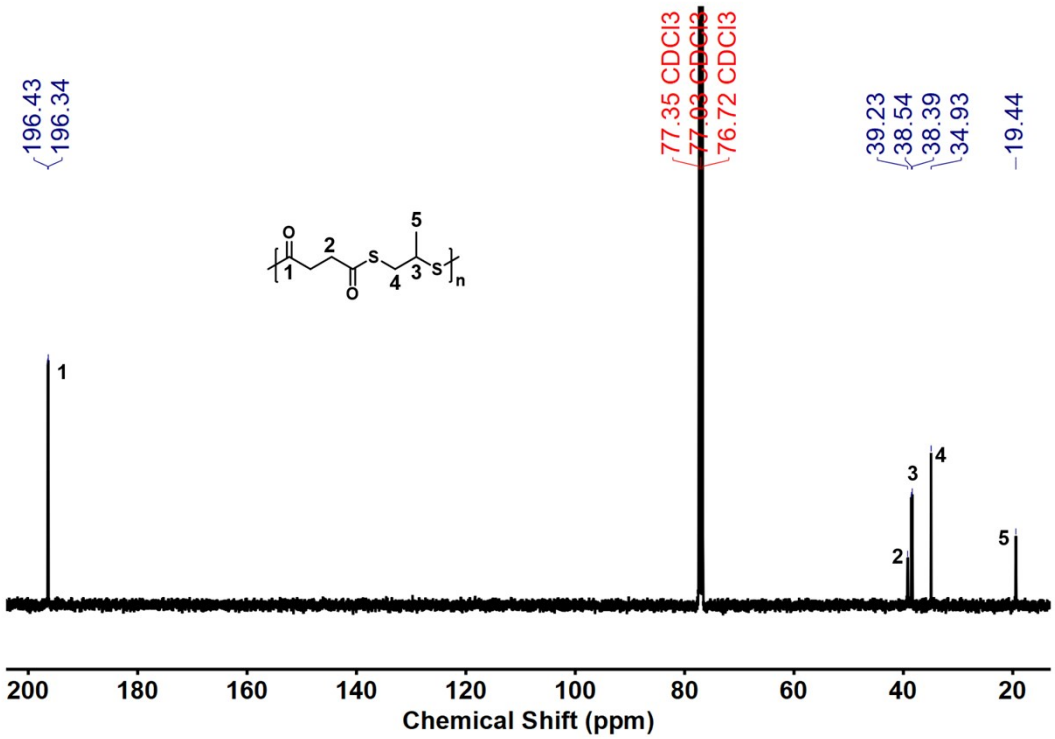



**Figure A2.** $^{13}C$ NMR spectrum of poly(STAH-*alt*-PS) in $CDCl_3$.

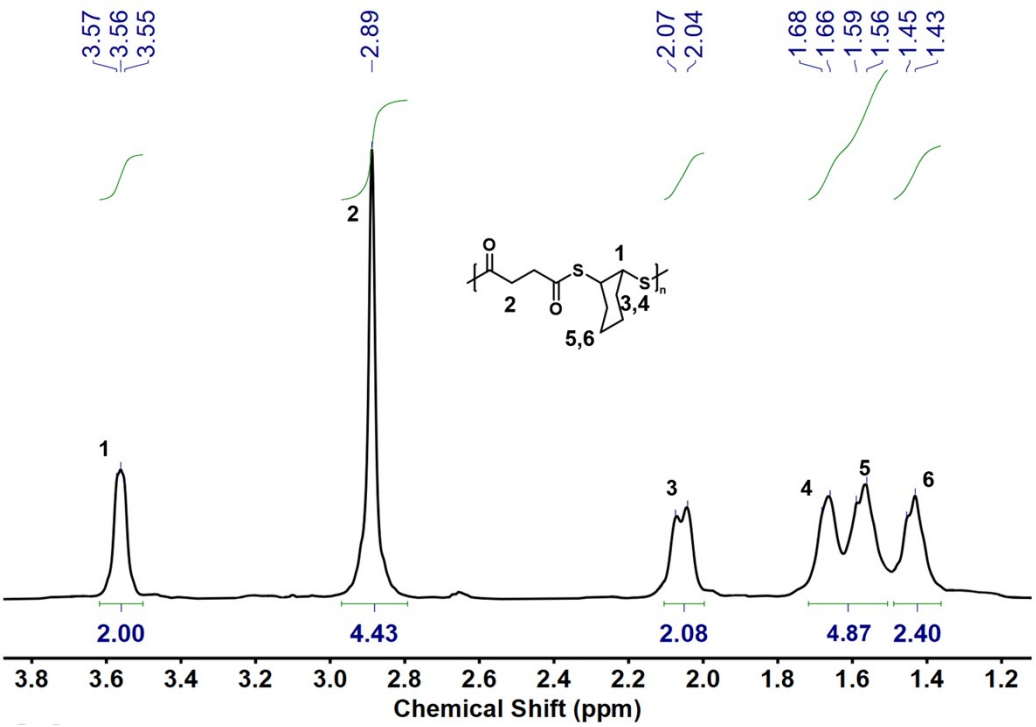



**Figure A3.** $^{1}$H NMR spectrum of poly(STAH-*alt*-CHS) in $CDCl_3$.

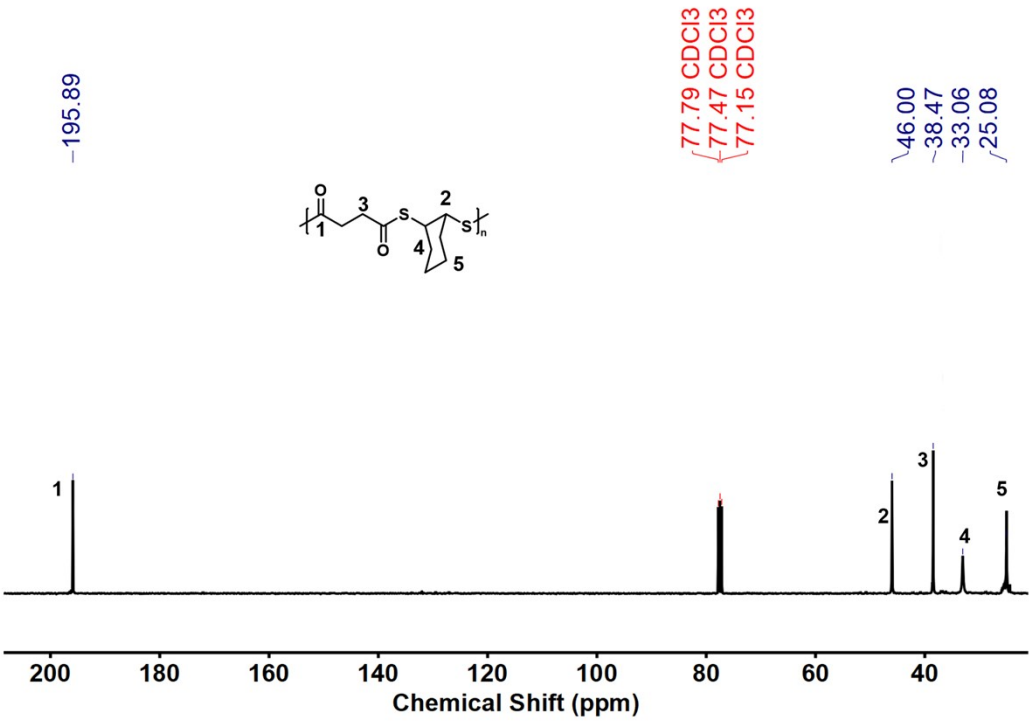



**Figure A4.** $^{13}$C NMR of poly(STAH-*alt*-CHS) in $CDCl_3$.

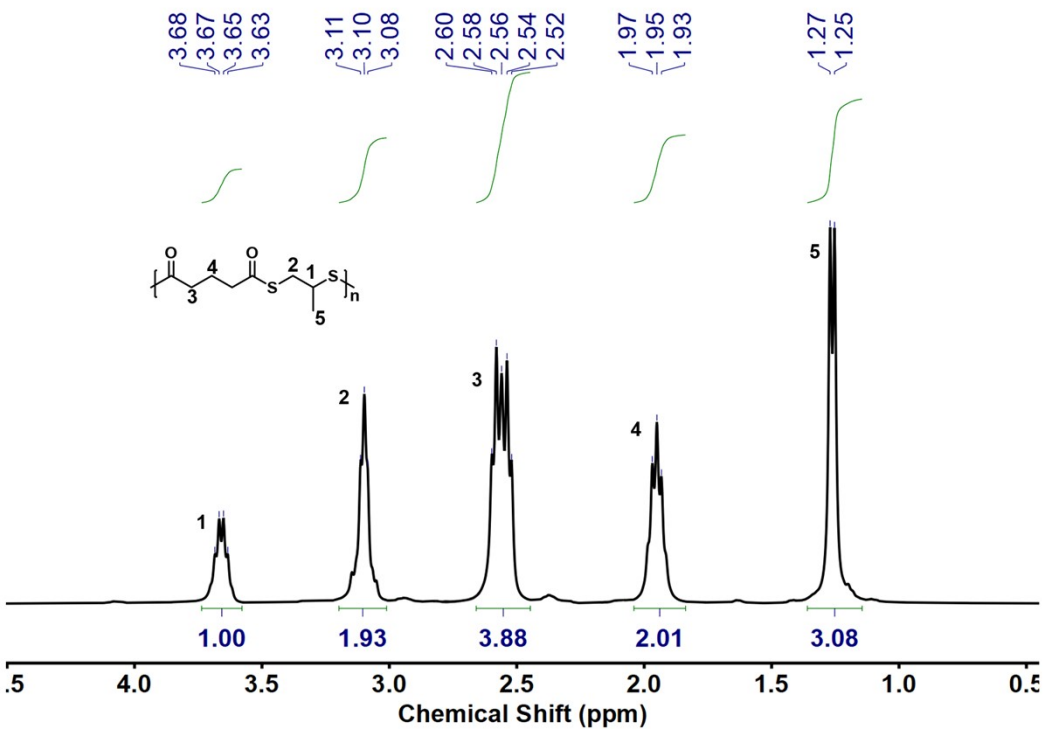



**Figure A5.** $^{1}$H NMR spectrum of poly(GTAH-*alt*-PS) in $CDCl_3$.

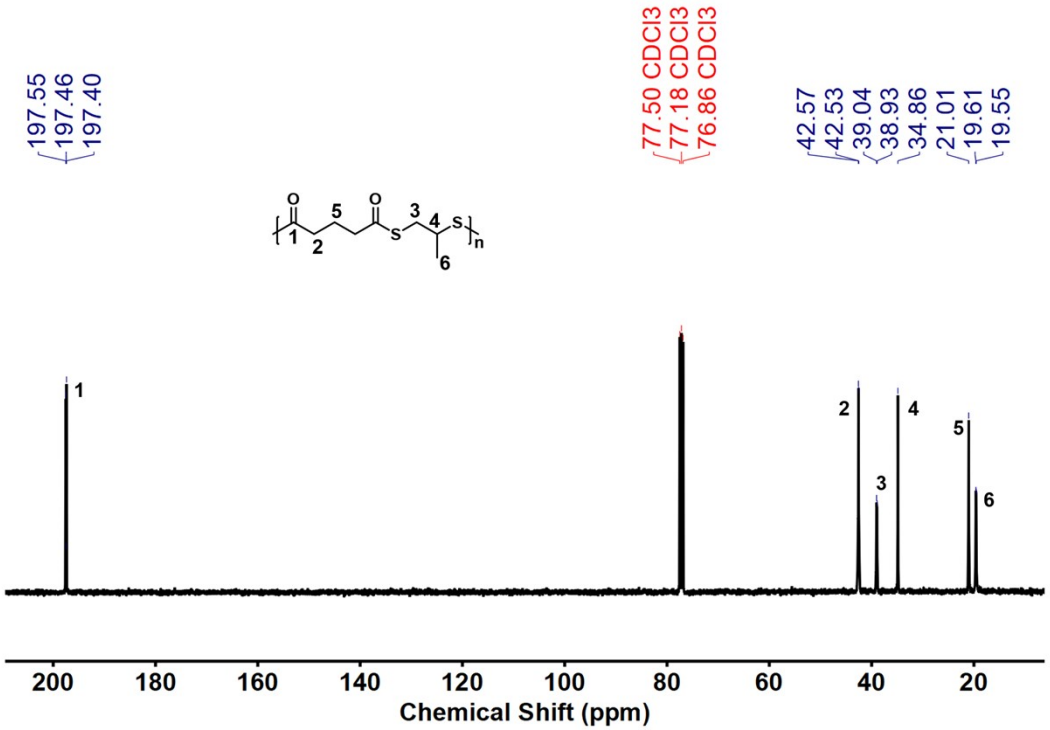



**Figure A6.** $^{13}$C NMR spectrum of poly(GTAH-*alt*-PS) in $CDCl_3$.

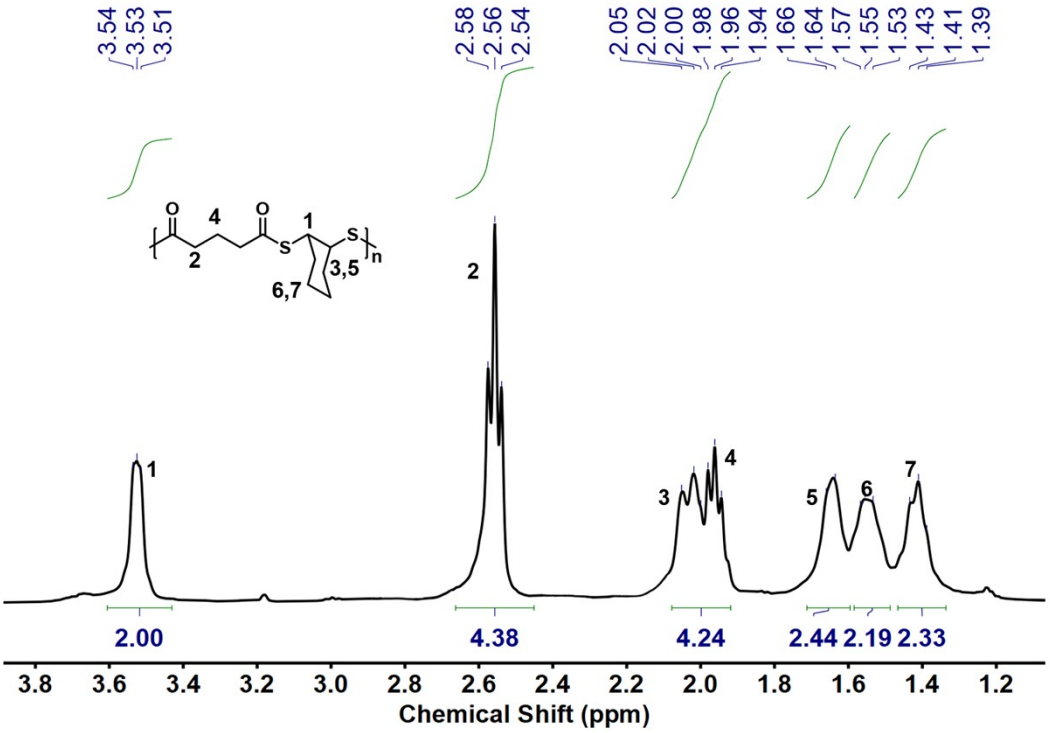



**Figure A7.** $^{1}$H NMR spectrum of poly(GTAH-*alt*-CHS) in $CDCl_3$.

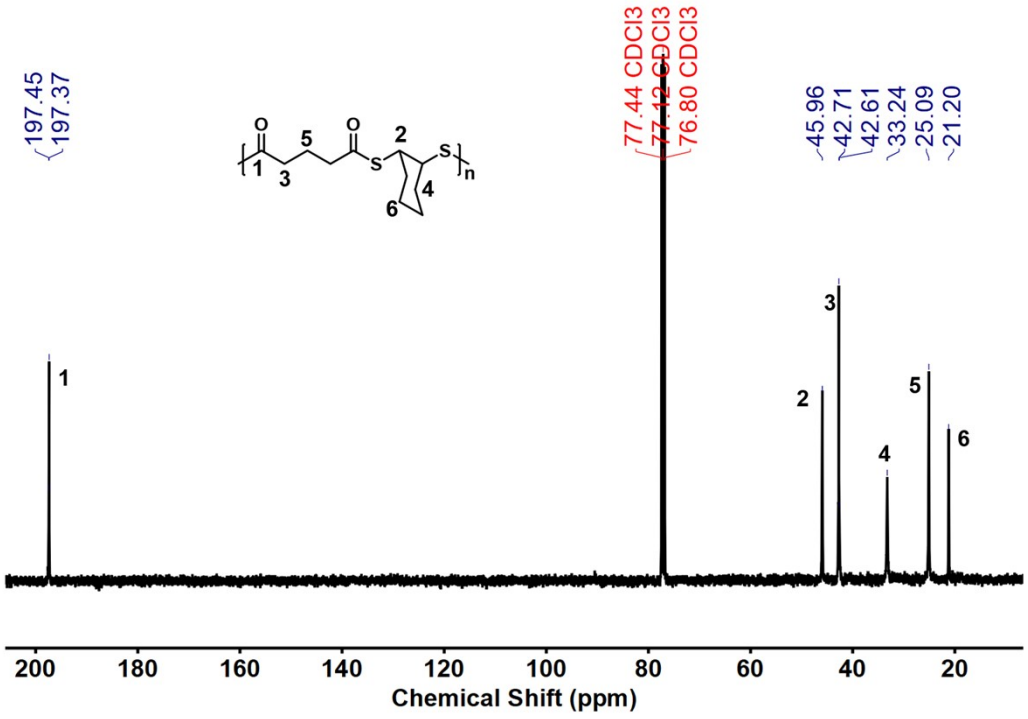



**Figure A8.** $^{13}$C NMR spectrum of poly(GTAH-*alt*-CHS) in $CDCl_3$.

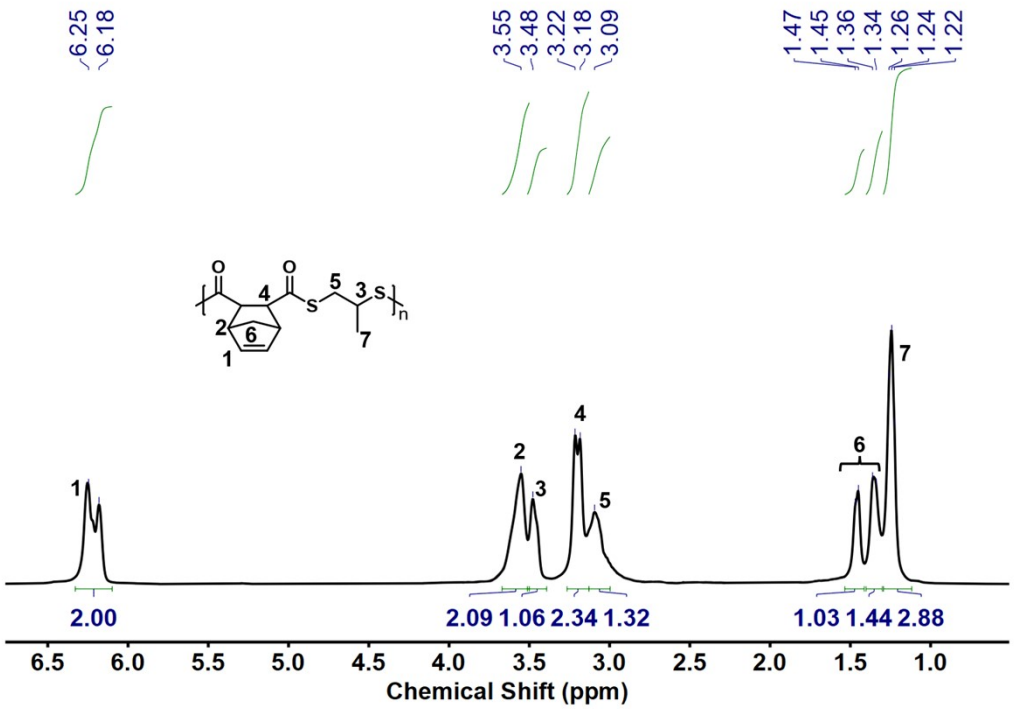



**Figure A9.** $^{1}$H NMR spectrum of poly(CTAH-*alt*-PS) in $CDCl_3$.

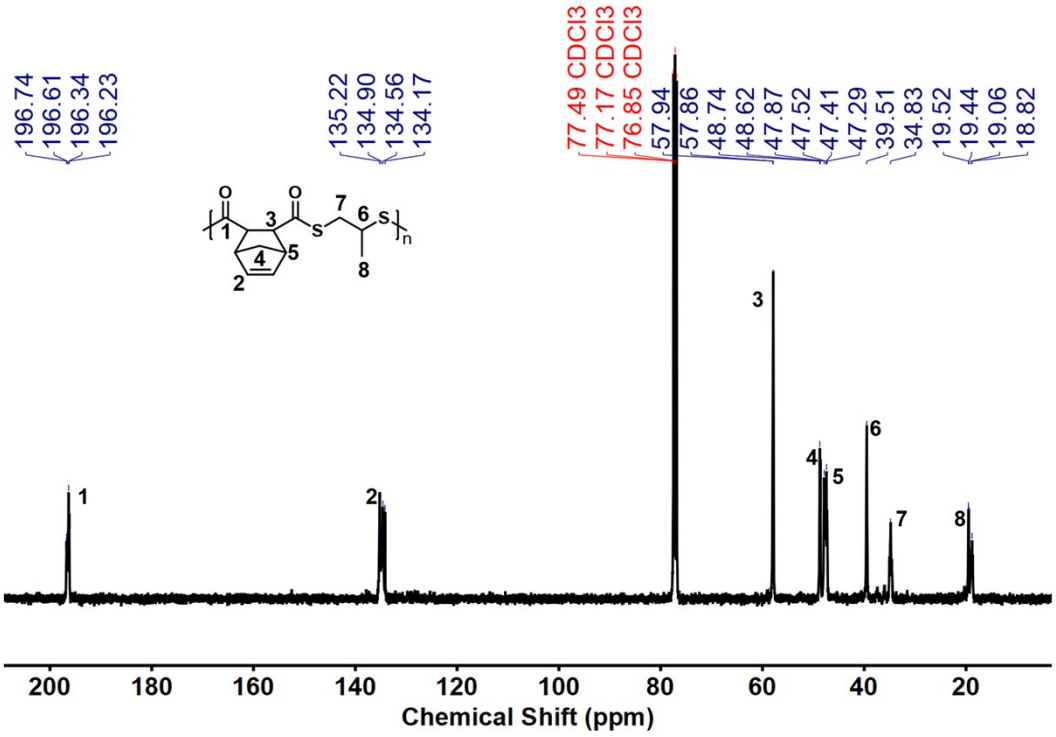



**Figure A10.** $^{13}$C NMR spectrum of poly(CTAH-*alt*-PS) in $CDCl_3$.

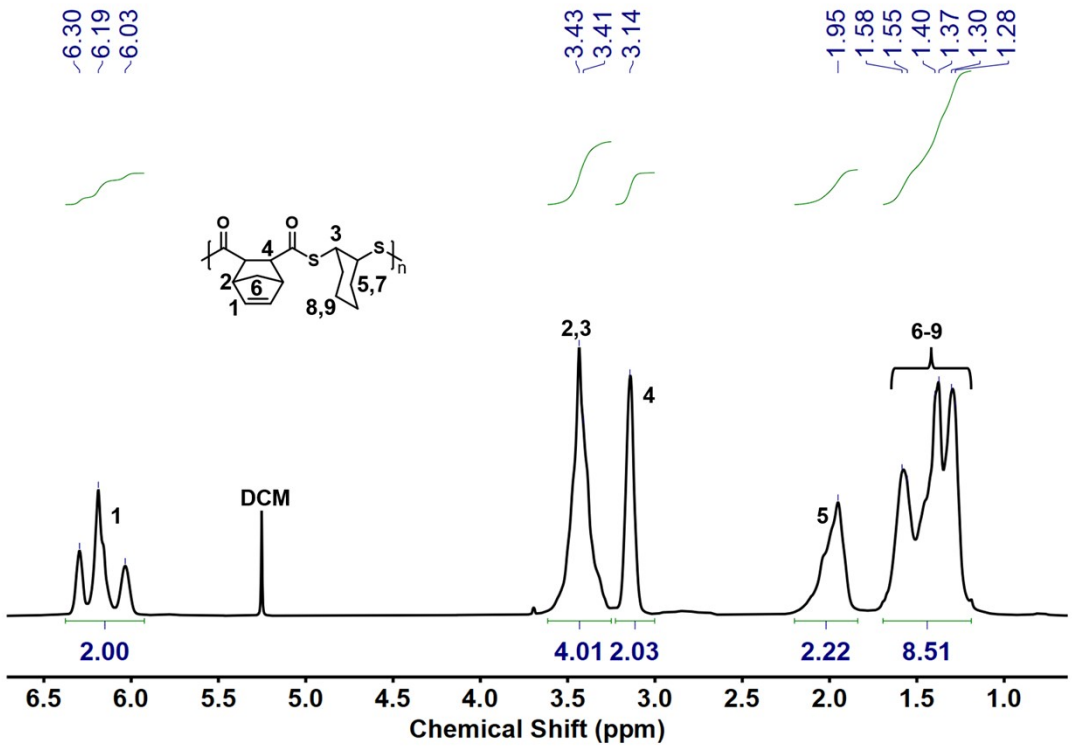



**Figure A11.** $^{1}$H NMR spectrum of poly(CTAH-*alt*-CHS) in $CDCl_3$.

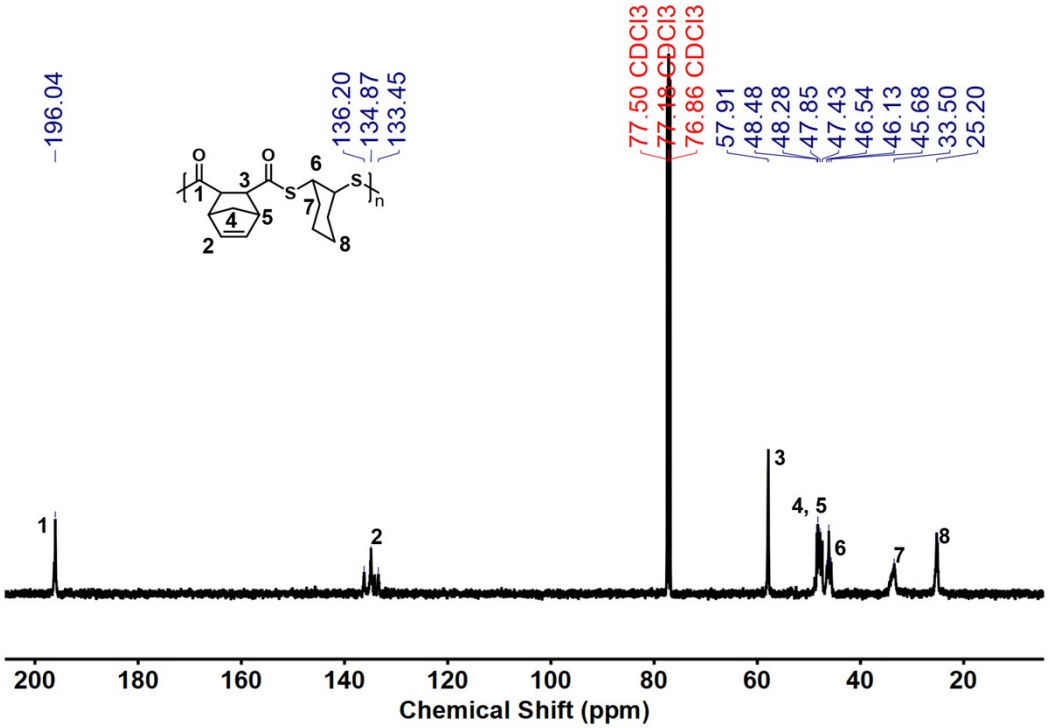



**Figure A12.** $^{13}$C NMR spectrum of poly(CTAH-*alt*-CHS) in $CDCl_3$.

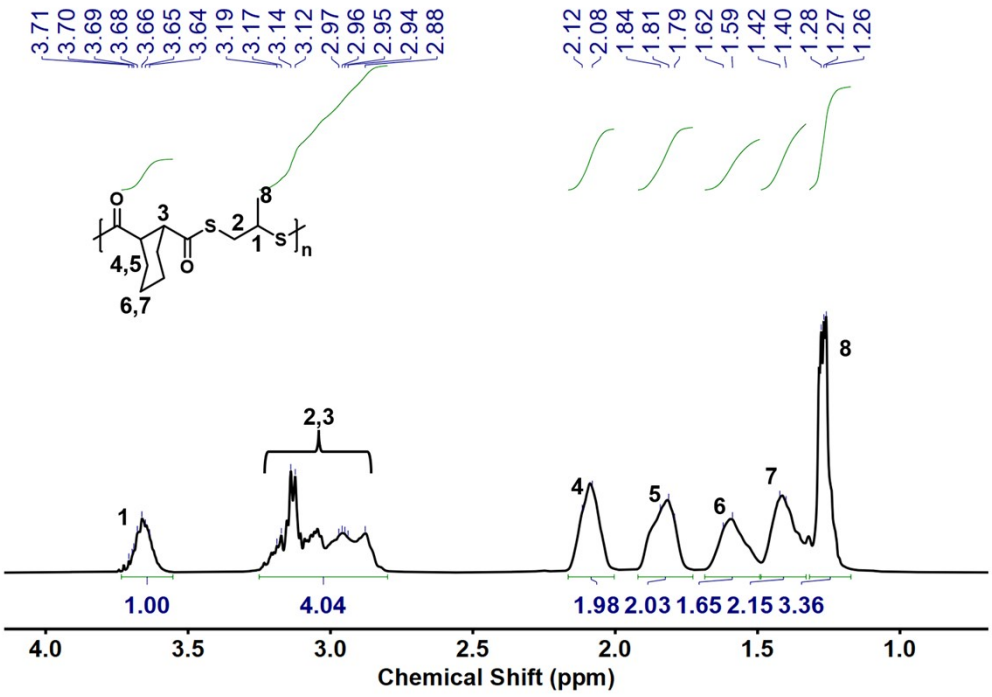



**Figure A13.** $^{1}$H NMR spectrum of poly(CHTH-*alt*-PS) in $CDCl_3$.

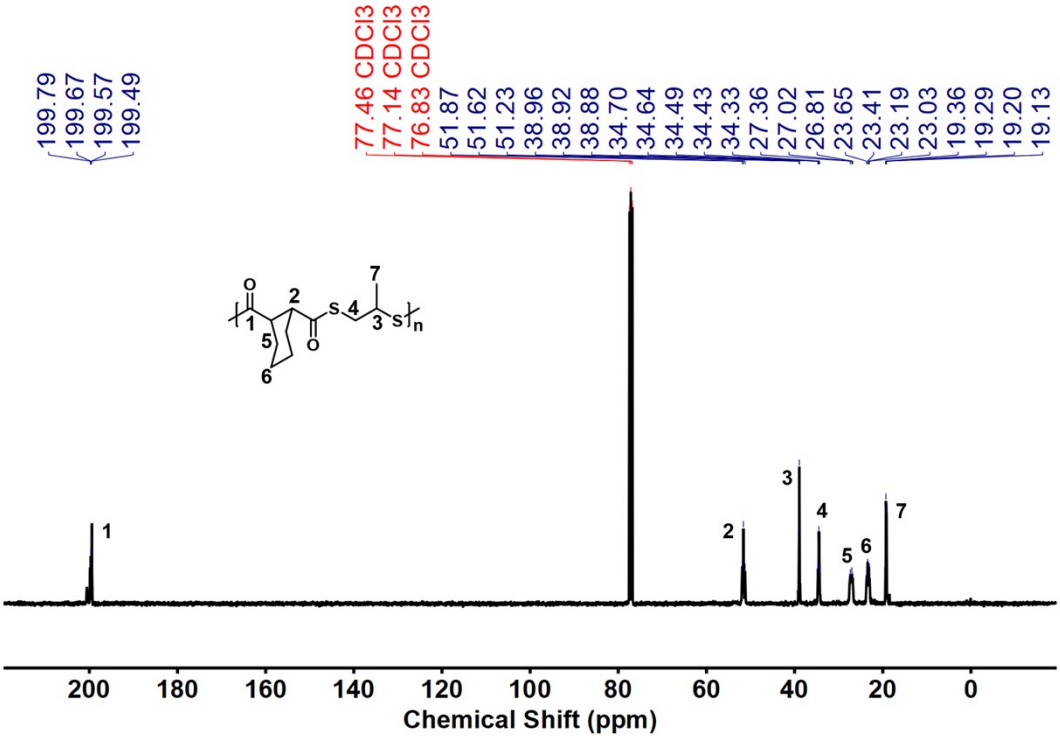



**Figure A14.** $^{13}$C NMR spectrum of poly(CHTH-*alt*-PS) in $CDCl_3$.

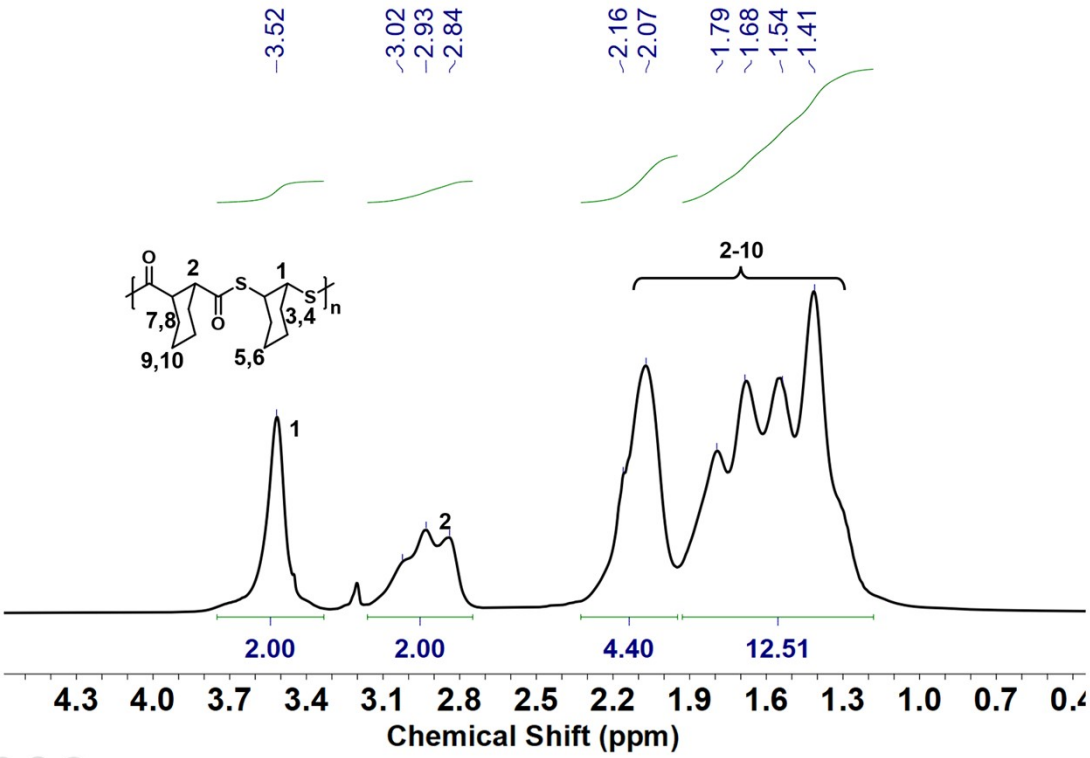



**Figure A15.** $^{1}$H NMR spectrum of poly(CHTH-*alt*-CHS) in $CDCl_3$.

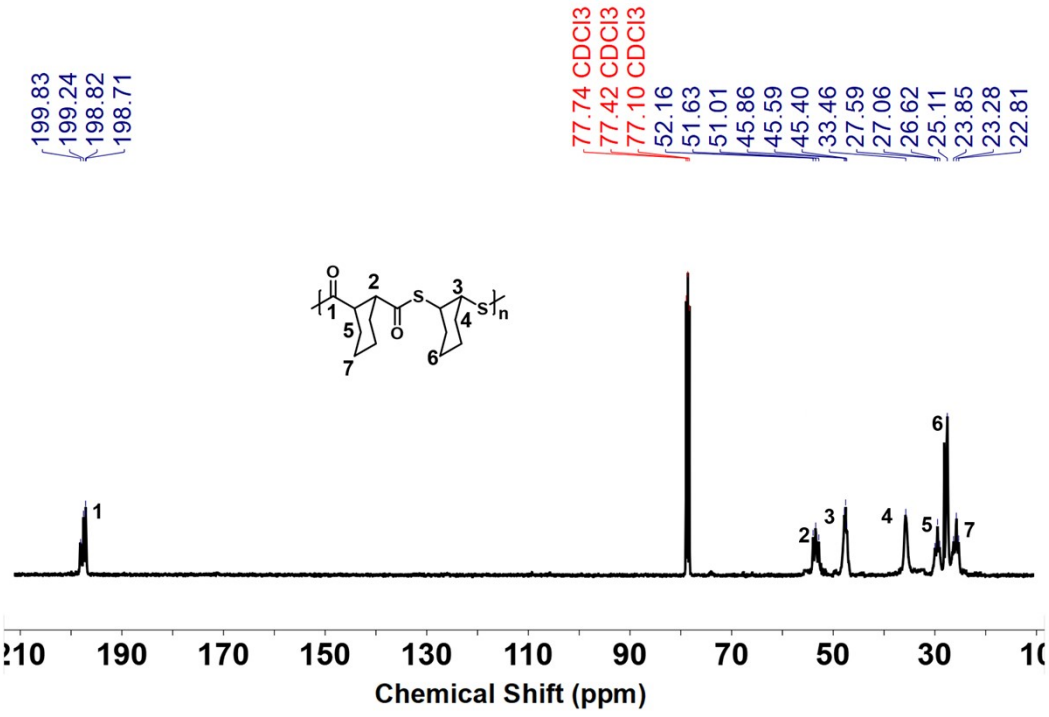



**Figure A16.** $^{13}$C NMR Spectrum of poly(CHTH-*alt*-CHS) in $CDCl_3$.

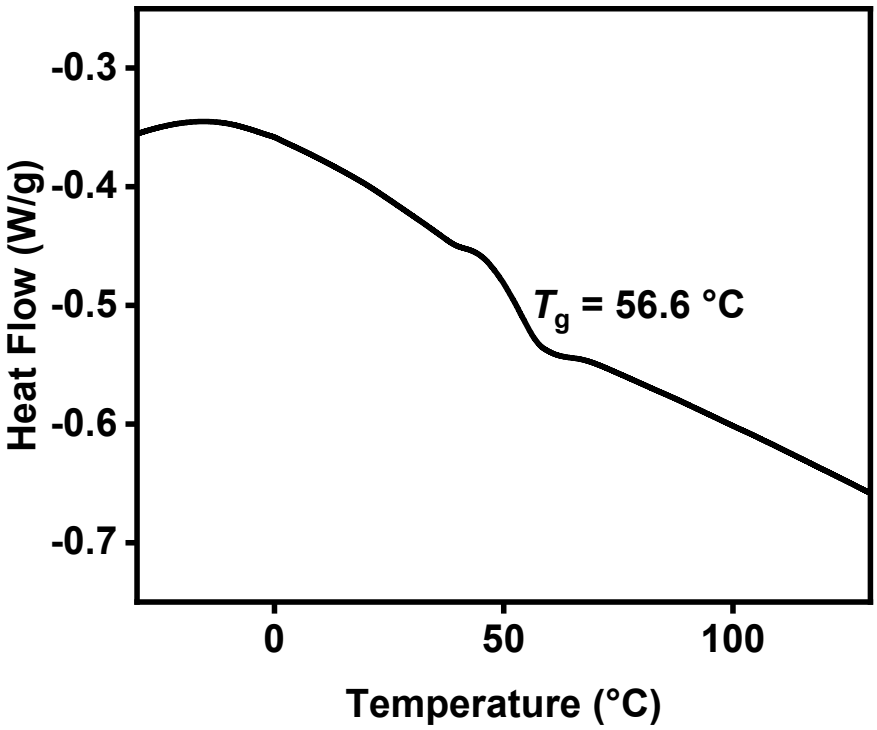



**Figure A17.** DSC thermogram of the poly(STAH-*alt*-CHS).

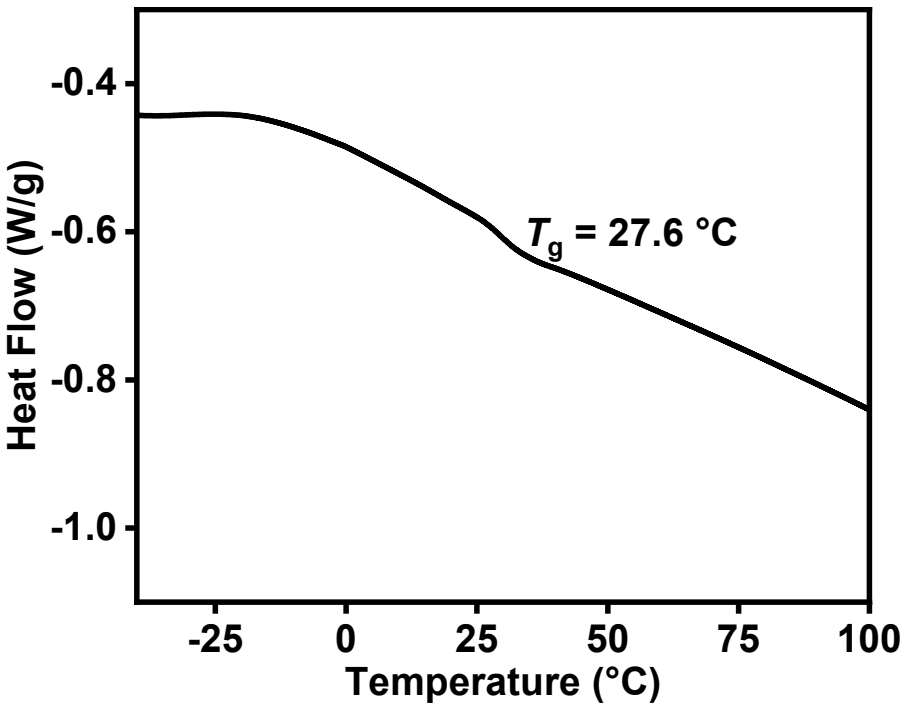



**Figure A18.** DSC thermogram of the poly(GTAH-*alt*-CHS).

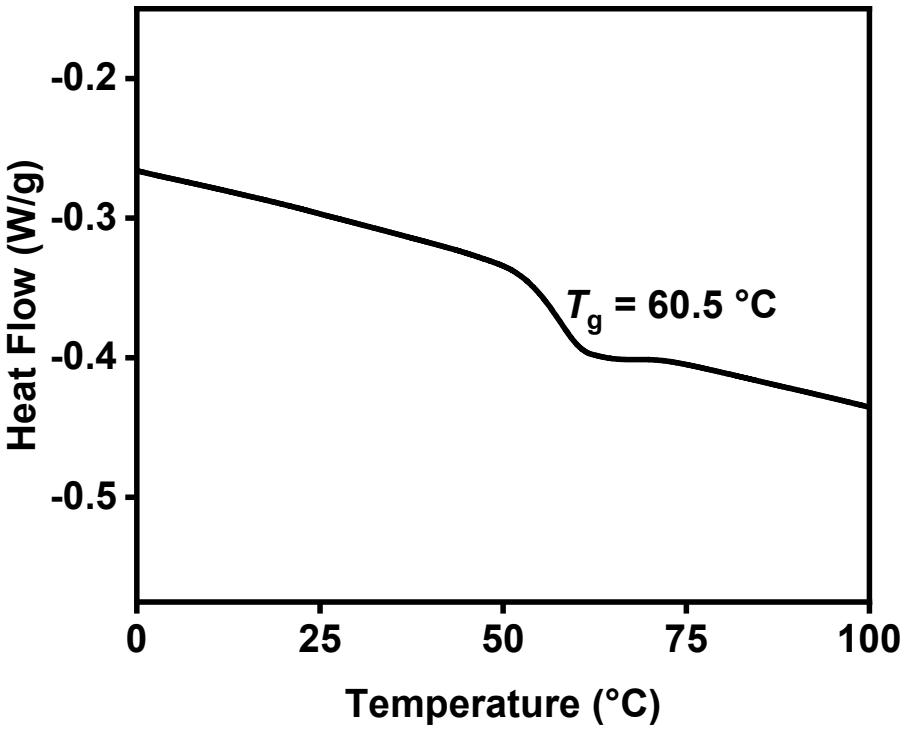



**Figure A19.** DSC thermogram of the poly(CHTH-*alt*-PS).

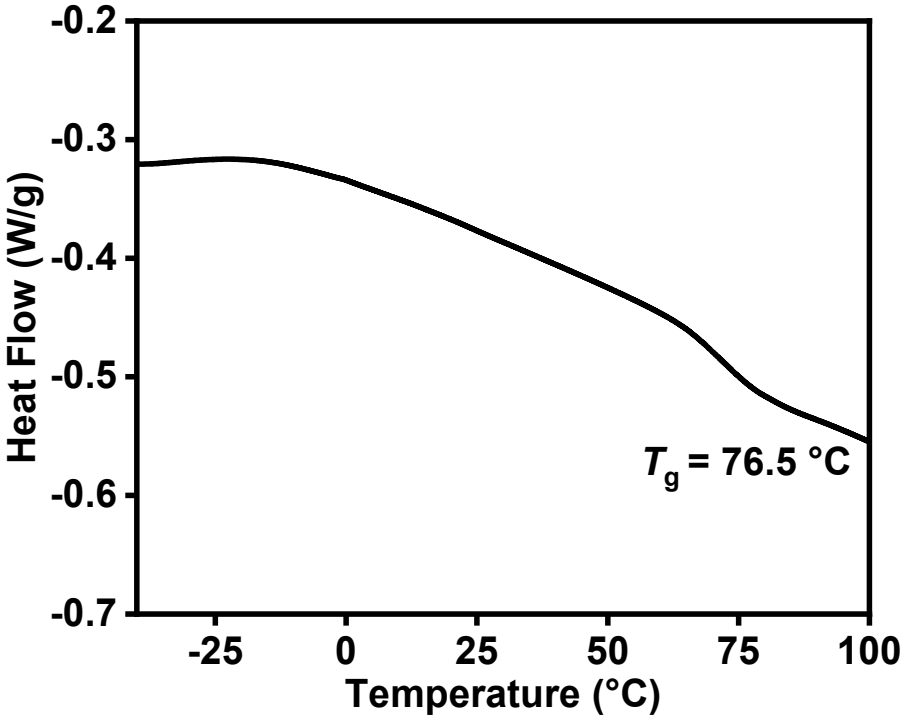



**Figure A20.** DSC thermogram of the poly(CHTH-*alt*-CHS).

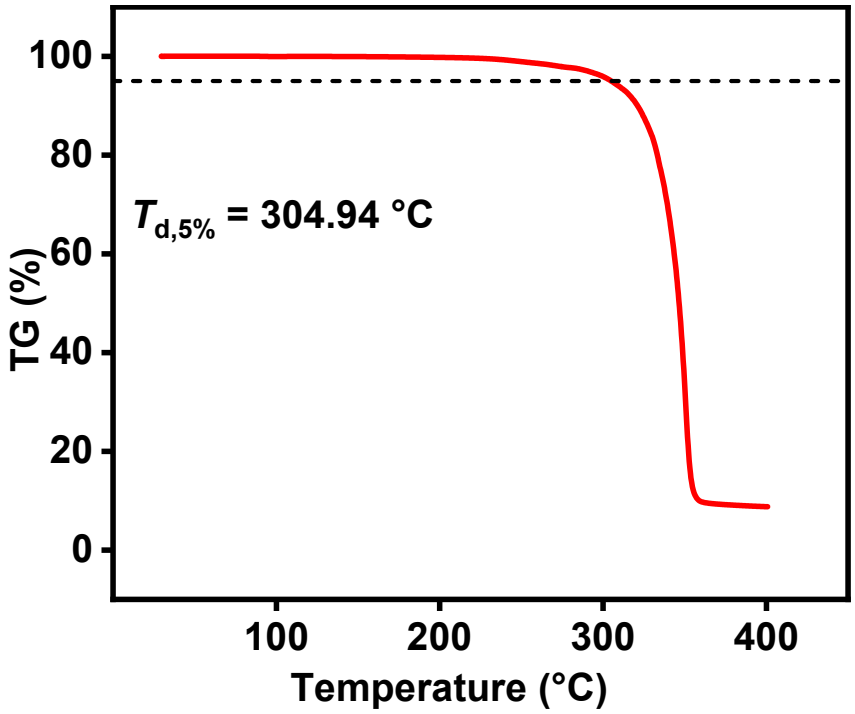



**Figure A21.** TGA curve of poly(STAH-*alt*-PS).

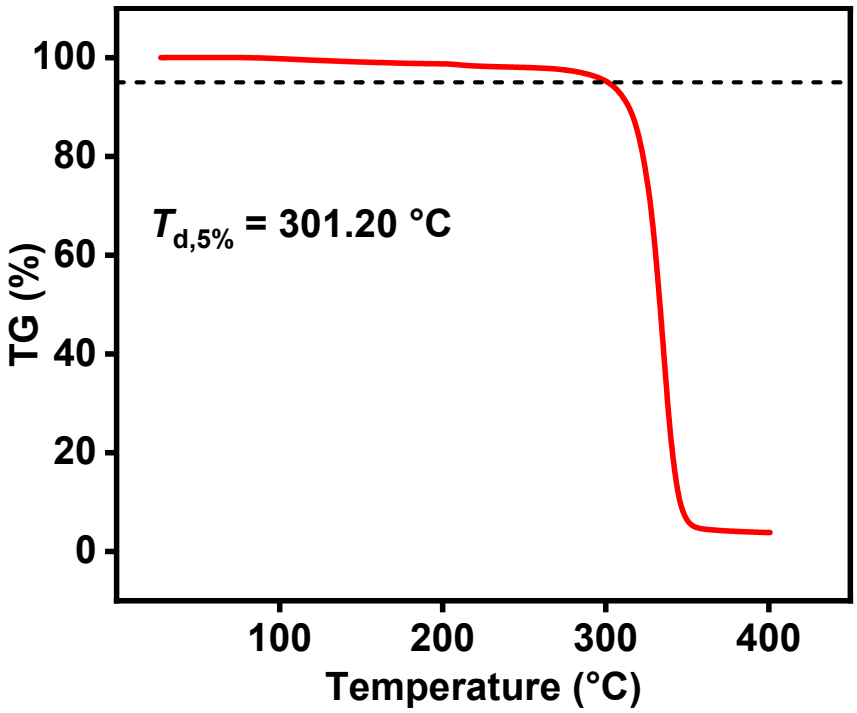



**Figure A22.** TGA curve of poly(STAH-*alt*-CHS).

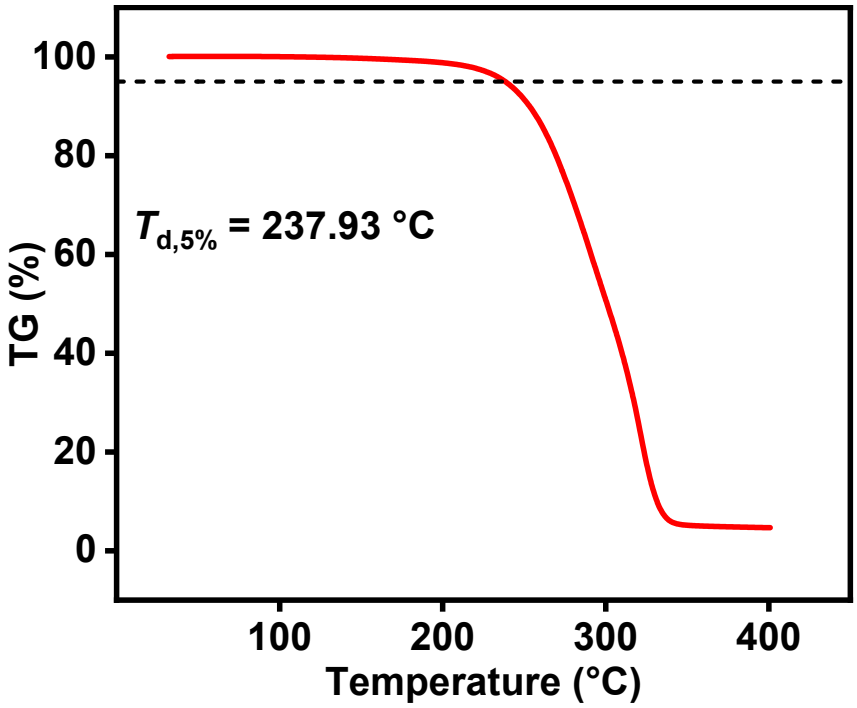



**Figure A23.** TGA curve of poly(GTAH-*alt*-PS).

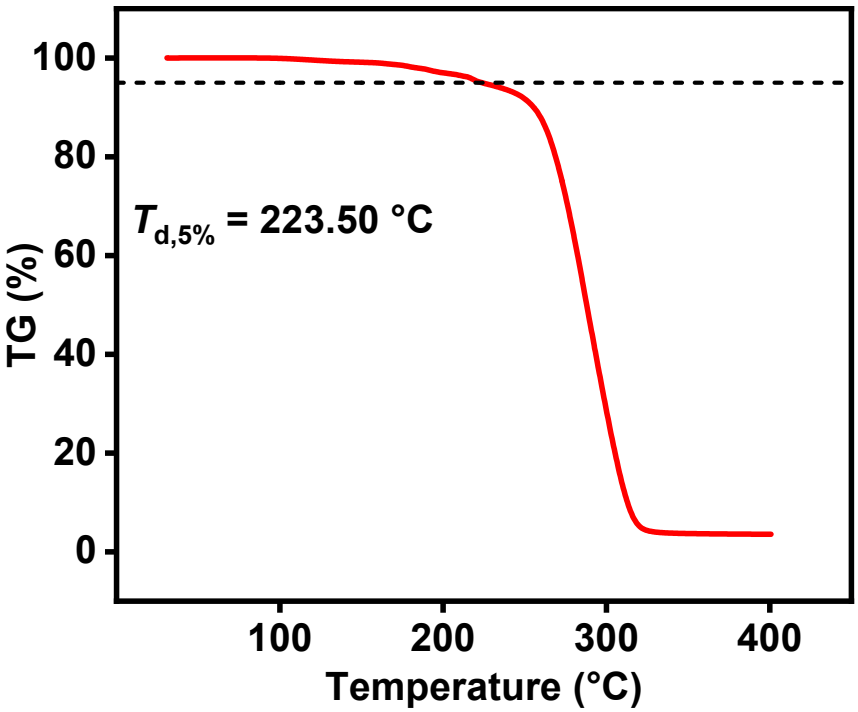



**Figure A24.** TGA curve of poly(GTAH-*alt*-CHS).

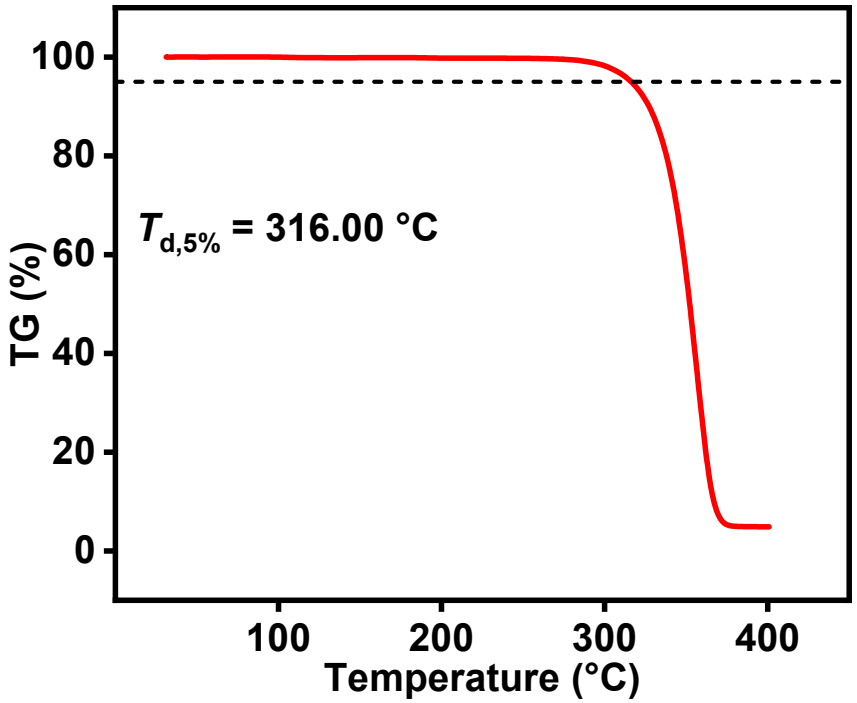



**Figure A25.** TGA curve of poly(CHTH-*alt*-PS).

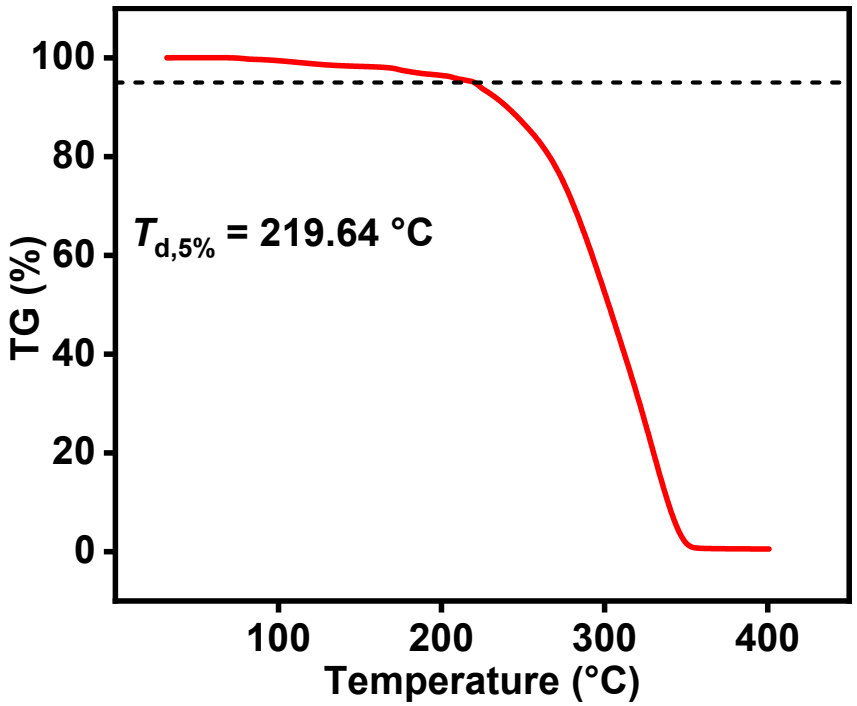



**Figure A26.** TGA curve of poly(CHTH-*alt*-CHS).

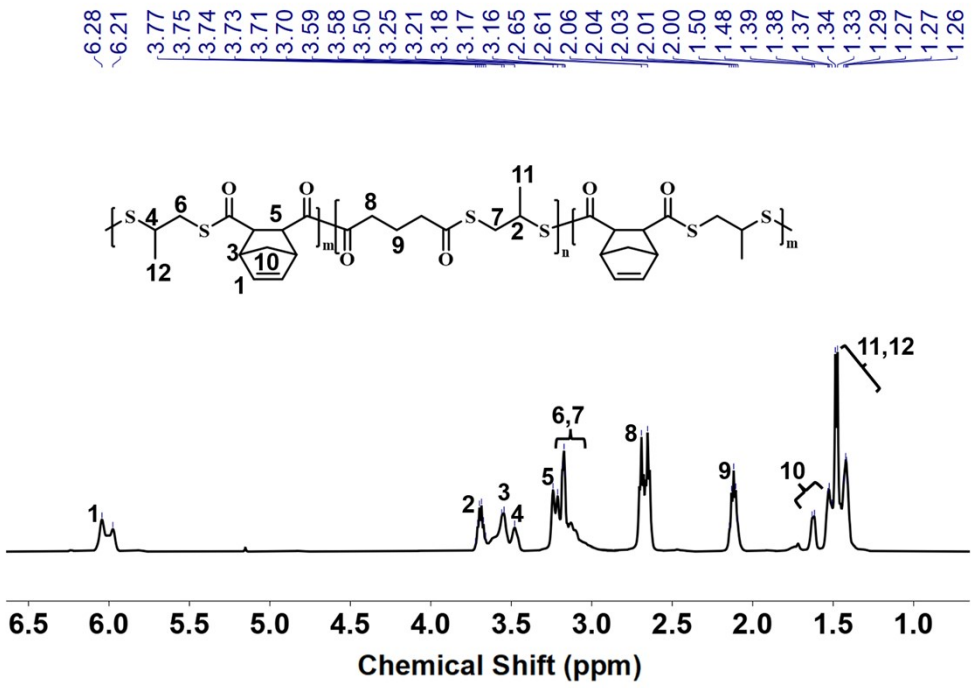



**Figure A27.** $^{1}$H NMR spectrum of block polythioester.

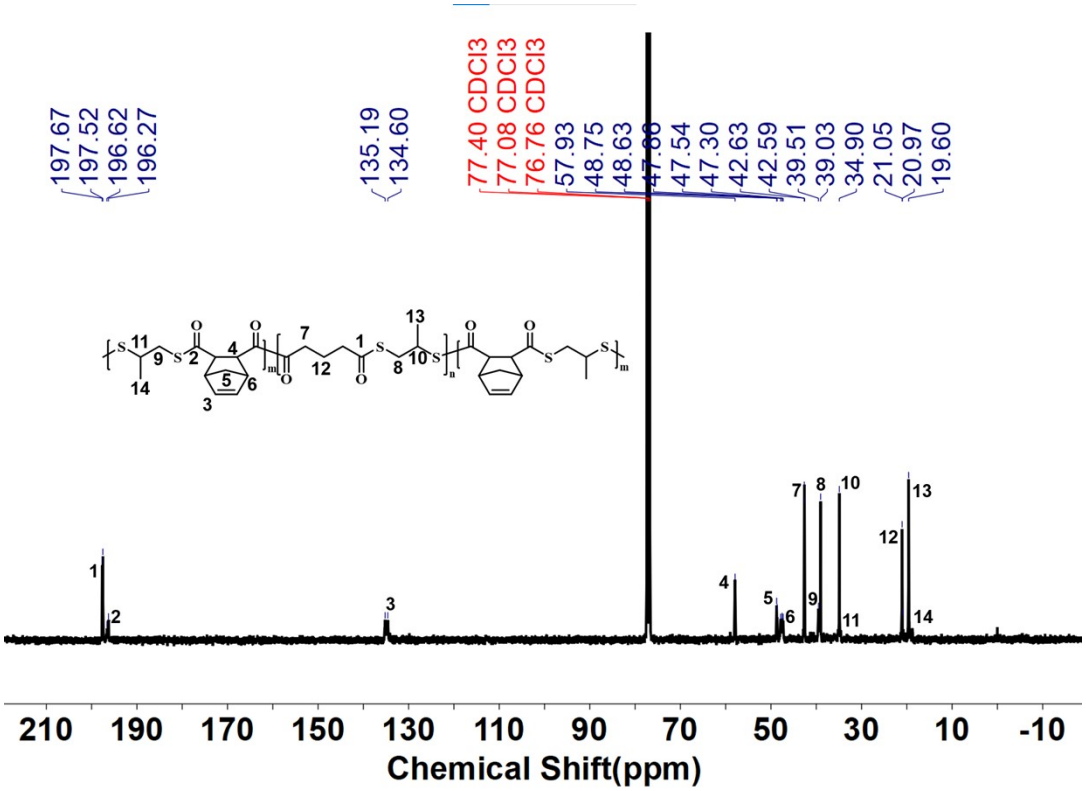



**Figure A28.** $^{13}$C NMR spectrum of block polythioester.