SUPPORTING INFORMATION

γ-Functionalized Thioether, Sulfoxide, and Sulfone AB Monomers for Tunable Aliphatic Polyesters

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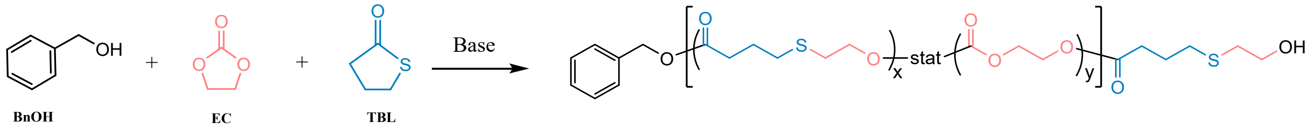
Content

1. Synthesis of Poly(thioether-*alt*-ester)s.



Scheme S1. Copolymerization of EC and TBL

Table S1. Experimental conditions and molecular characteristics of copolymerization

Run	ROH: Base: Epoxide: TBL	Base	Time (h)	Temp (°C)	Cv[a](%) TBL	Cv[b](%) EC	$M_{n,th}$[c] (g mol⁻¹)	$M_{n,\,NMR}$ (g mol⁻¹)	$M_{n,\,SEC}$[d] (g mol⁻¹)	Đ	Cyclic carbonate units[e] (%)
1	1:1:50:50	DMAP	24	100	77	99	5729	3141	8200	1.92	8
2	1:1:50:50	BEMP	24	100	51	75	3836	3093	9600	1.83	12
3	1:1:50:50	$tBuP_4$	24	100	98	95	7052	11915	8500	3.90	5
4	1:1:50:50	DBU	24	100	100	99	5202	6765	9000	2.04	7
5	1:140:140	DBU	24	100	100	100	26737	15694	10000	2.24	6

[a] TBL conversion was determined by ^1H NMR in DMSO-d_6 of the reaction

[b] EC conversion was determined by ^1H NMR in DMSO-d_6 of the reaction

[c] Mn,th is calculated considering a perfectly alternating structure initiated by benzyl alcohol according to the following equation:

$Mn,theo = M_{benzy!alcohol} + (M_{TBL} + M_{EO})$ x X^0_n limiting monomer x p_{TBL}

[d] Determined by SEC (DMF, 45°C, poly(methyl methacrylate) standards).

[e]

$$Cv\,[Cyclic\ carbonate\ unitse\ (\%)] = \frac{Xn,cy}{Xn,TL + Xn,EO} = \frac{\frac{I(k+l)/4}{Ia/5}}{\frac{Ie/2}{Ia/5} + \frac{Ih/2}{Ia/5}}$$

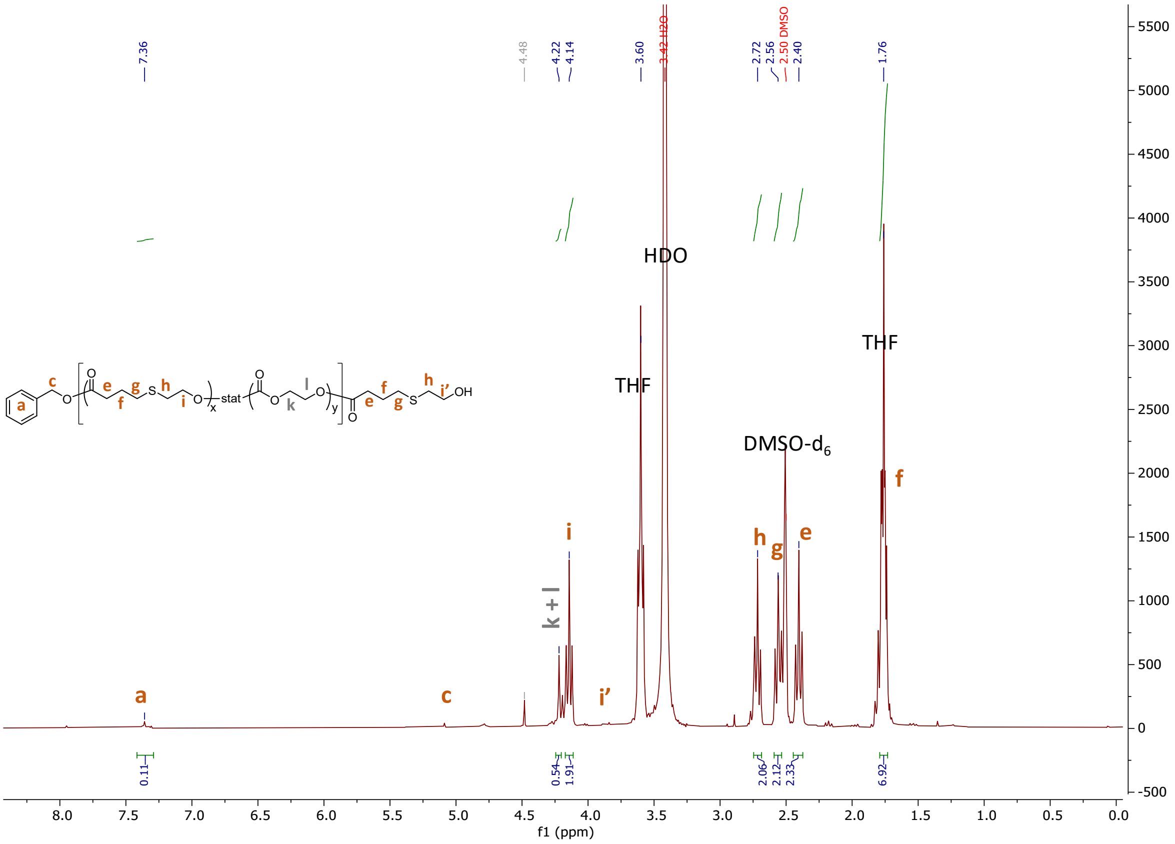


Figure S1. ^{1}H NMR spectrum in DMSO-d6 of PTE initiated by benzyl alcohol – DBU system in bulk at 100°C.

2. Depolymerization of PTE.

Table S2. Degradation experiment of PTE-EC in NaOH (0.1mol/L)

Run	Time (h)	$M_{n, SEC}$ (g mol^{-1})	Degradation [1] (%)
1	0	10000	0
2	2	3500	50
3	4	3100	56
4	6	1000	62
5	8	500	68
6	16	<50	93

[1] The percentage of degradation was calculated by ^{1}H NMR according to the following equation

$$\%\mathrm{deg} = \left(1 - \frac{I_i}{I_{c'+e}}\right) \times 100$$

.

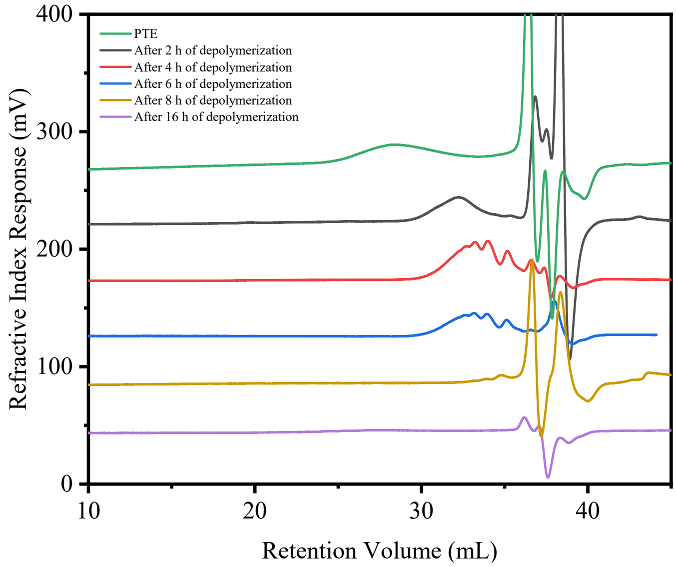


Figure S2. SEC chromatogram monitoring of PTE depolymerization by a 1 mol·L^{-1} NaOH solution in a THF/MeOH mixture (1:1, v/v).

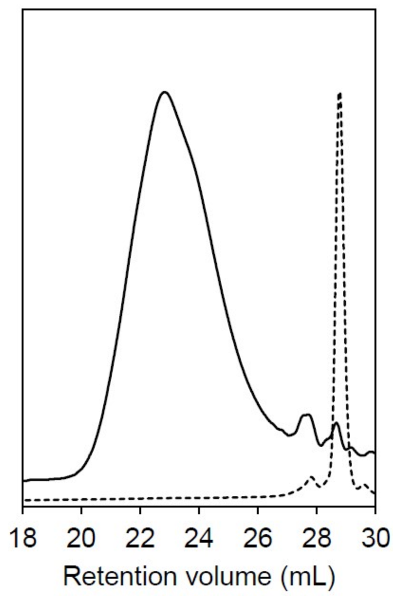


Figure S3. SEC chromatograms in THF at 40°C of PTE (solid line) and its degradation product (dotted line)

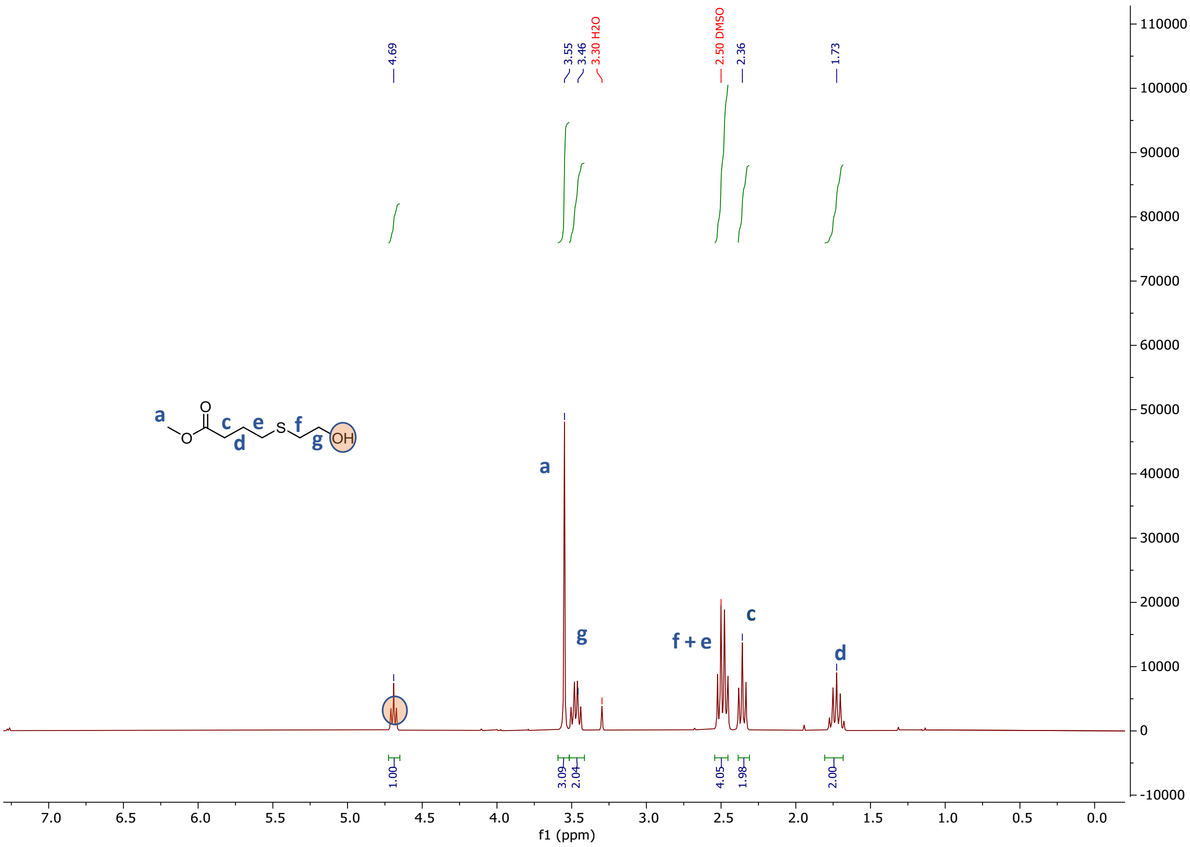


Figure S4. ^{1}H NMR spectrum of MTB after purification in DMSO-d6

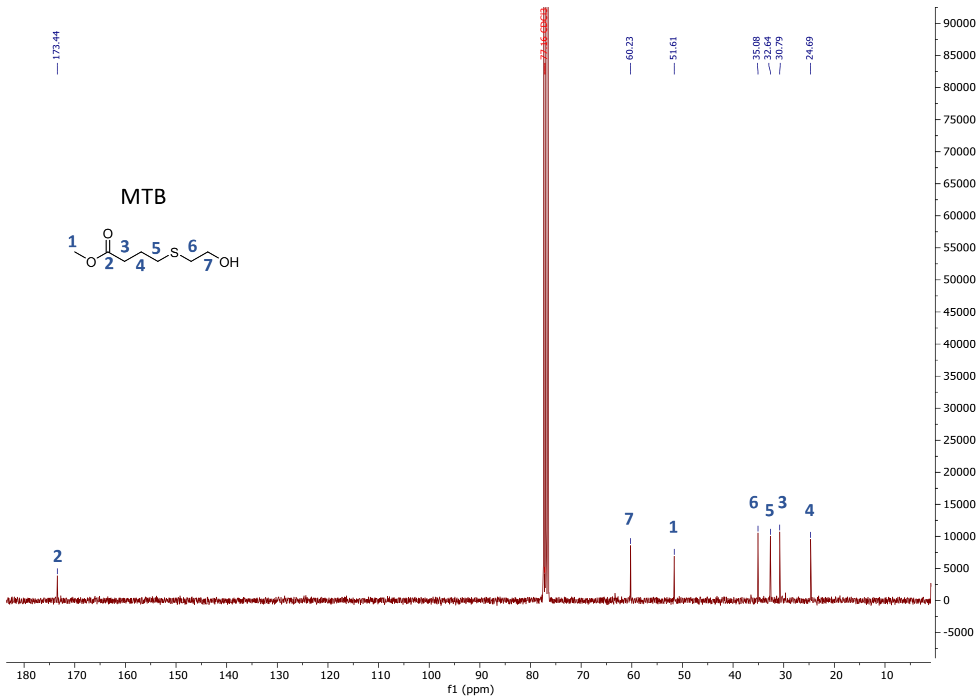


Figure S5. ^{13}C NMR spectrum of MTB in $CDCl_3$

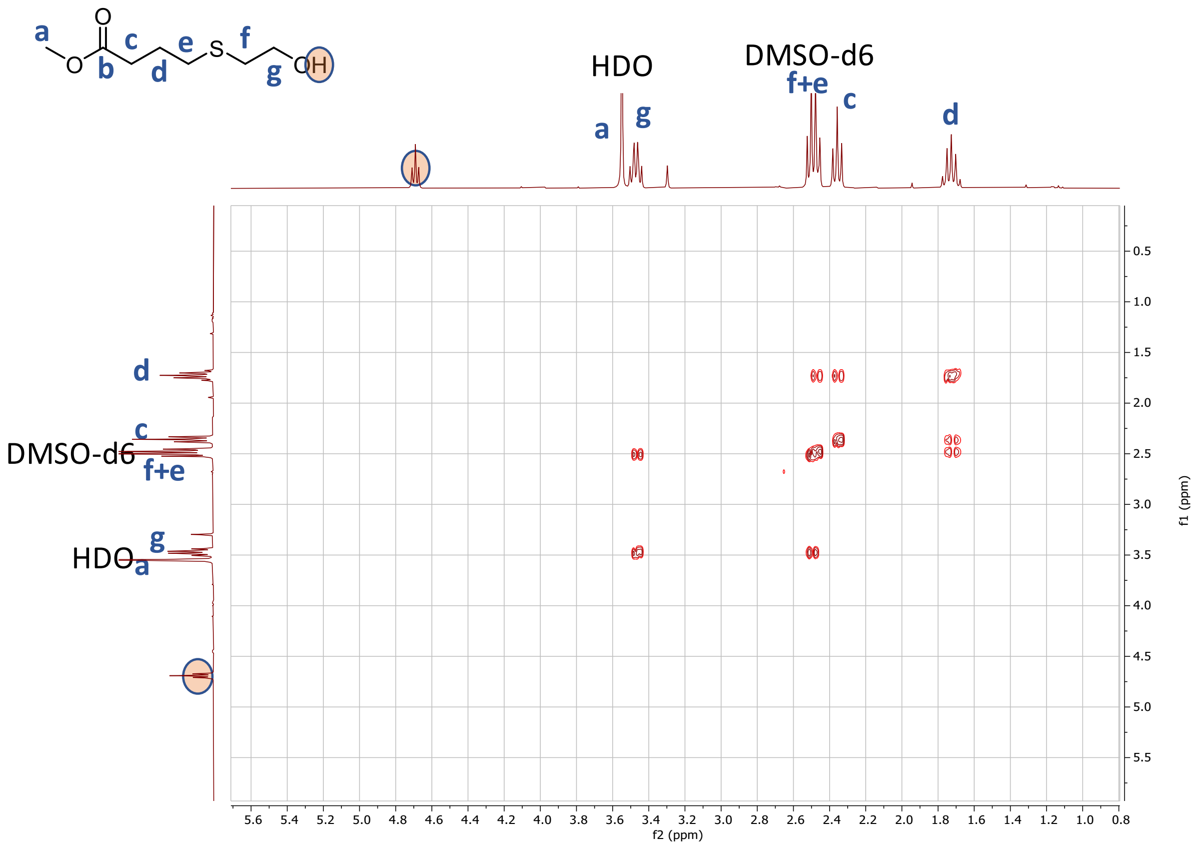


Figure S6. COSY spectrum of MTB in DMSO-d6

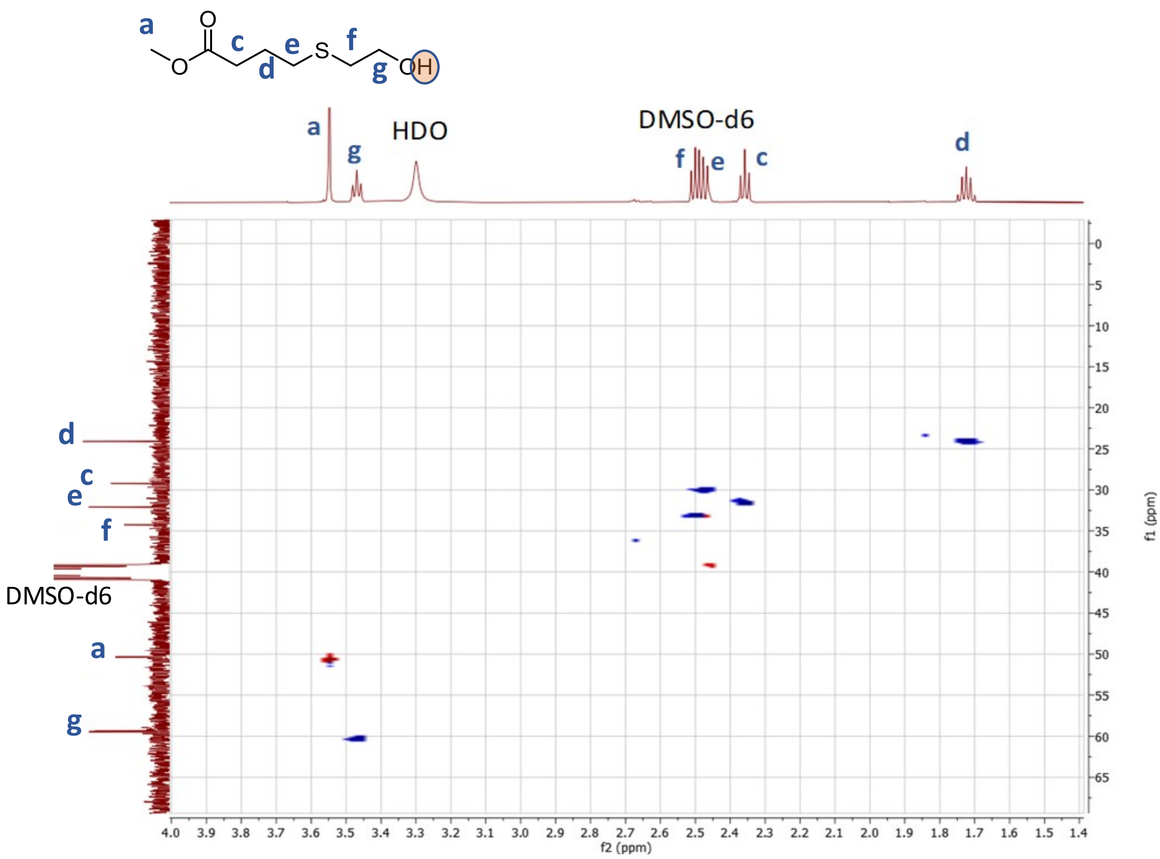


Figure S7. HSQC spectrum of MTB in DMSO-d6

3. AB monomer oxidation

3.1. Before purification

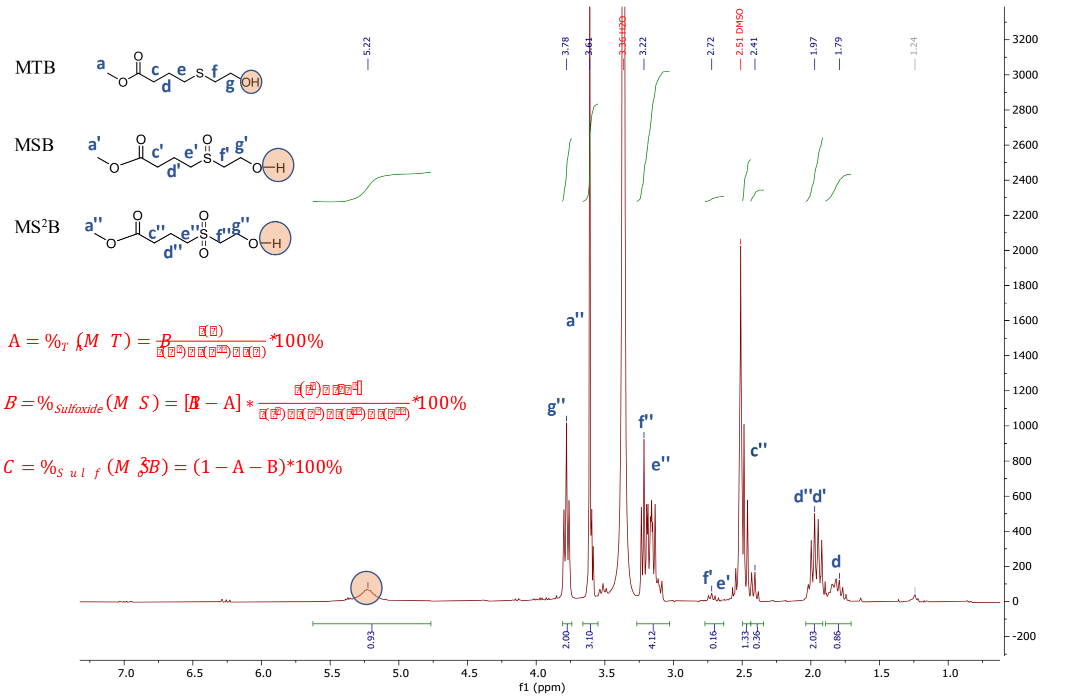


Figure S8. ^1H NMR spectrum of MTB oxidized by 20eq NaOCl before purification in DMSO-d6

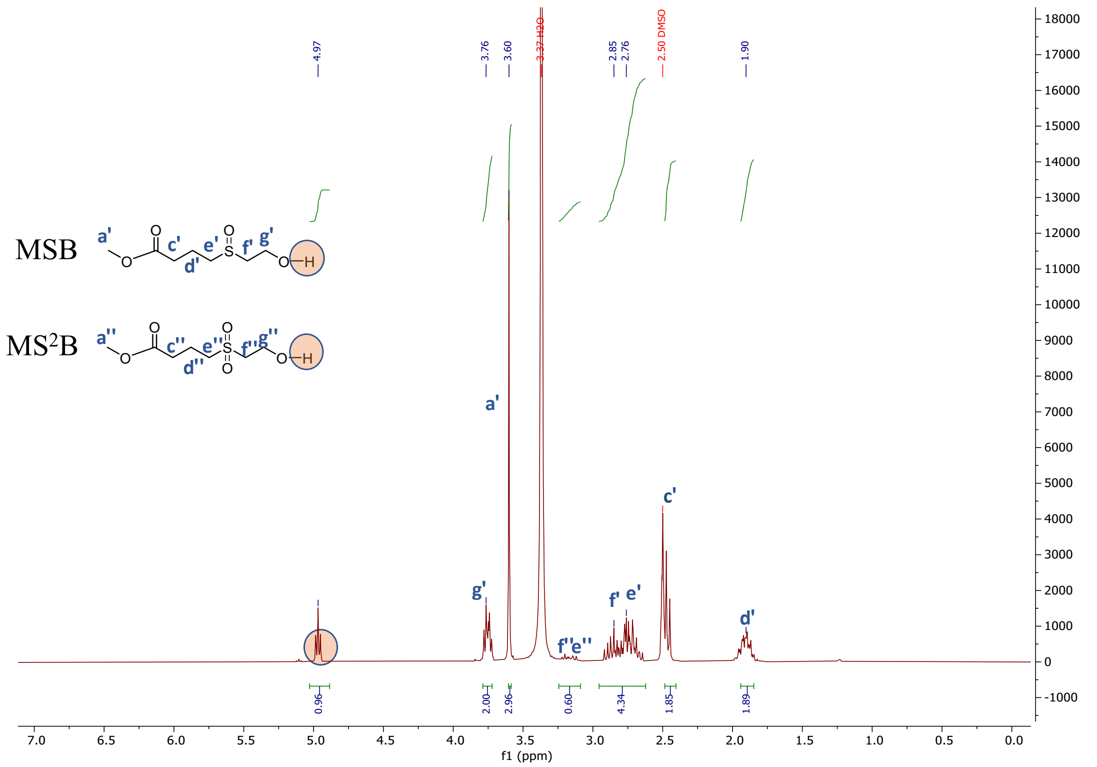


Figure S9. ^1H NMR spectrum of MTB oxidized by 2eq H_2O_2 before purification in DMSO-d6

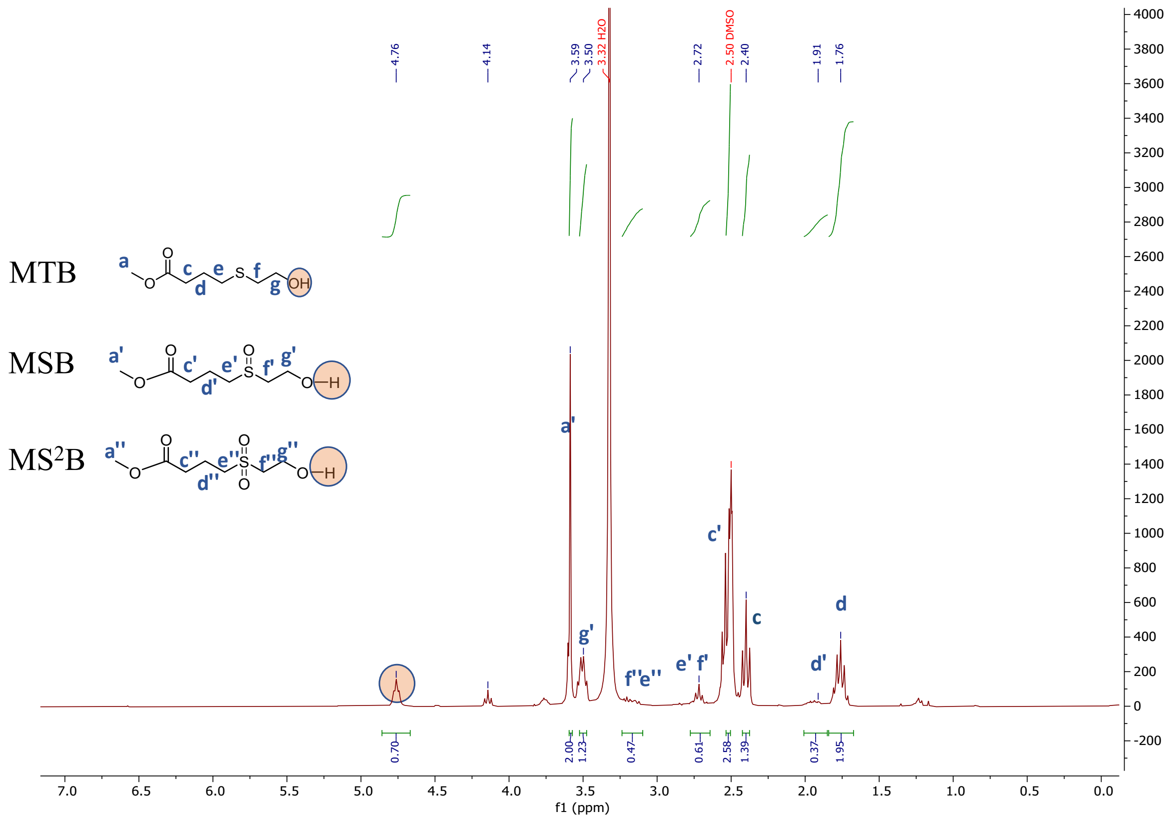


Figure S10. [1]H NMR spectrum of MTB oxidized by 2eq NaOCl before purification in DMSO-d6

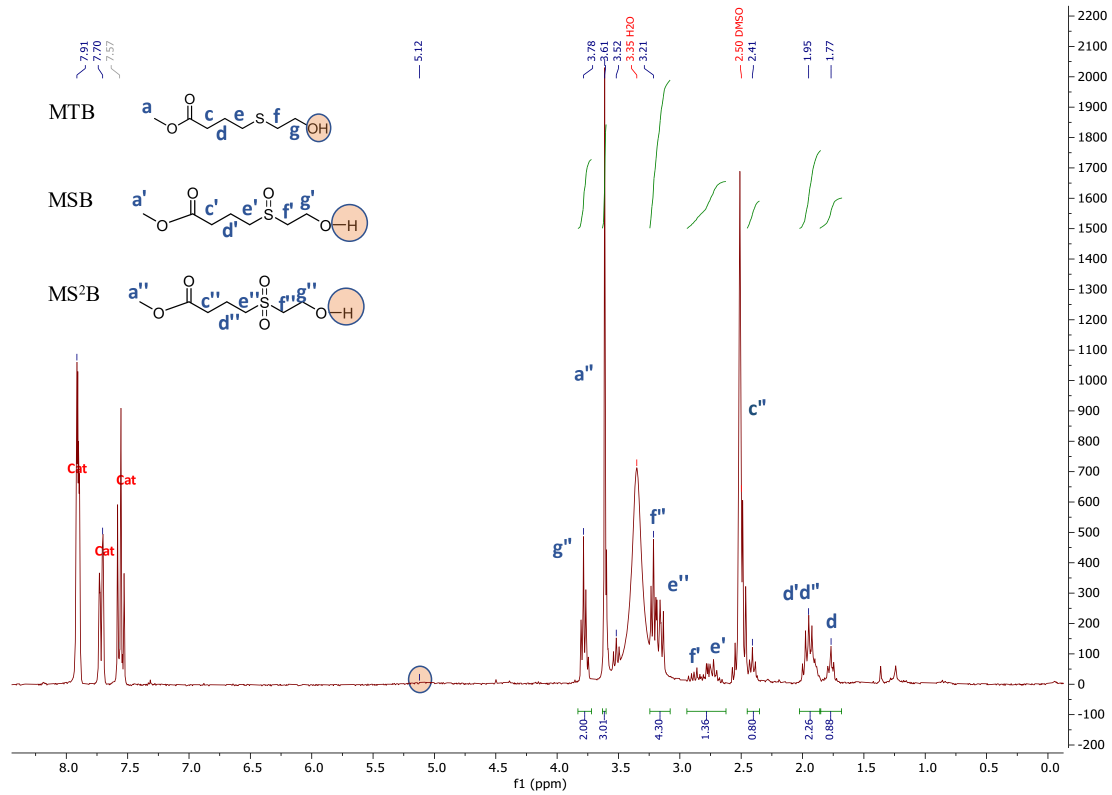


Figure S11. [1]H NMR spectrum of MTB oxidized by 2eq M-CPBA before purification in DMSO-d6

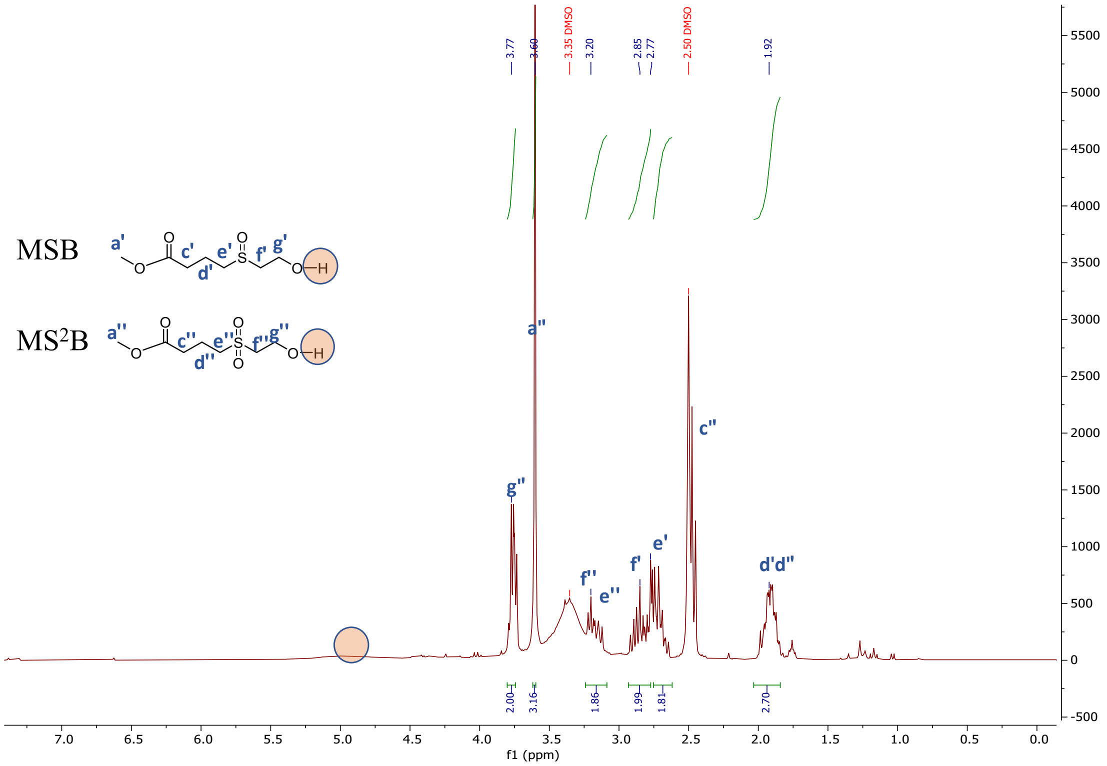


Figure S12. ^{1}H NMR spectrum of MTB oxidized by 20eq H_2O_2 before purification in DMSO-d6

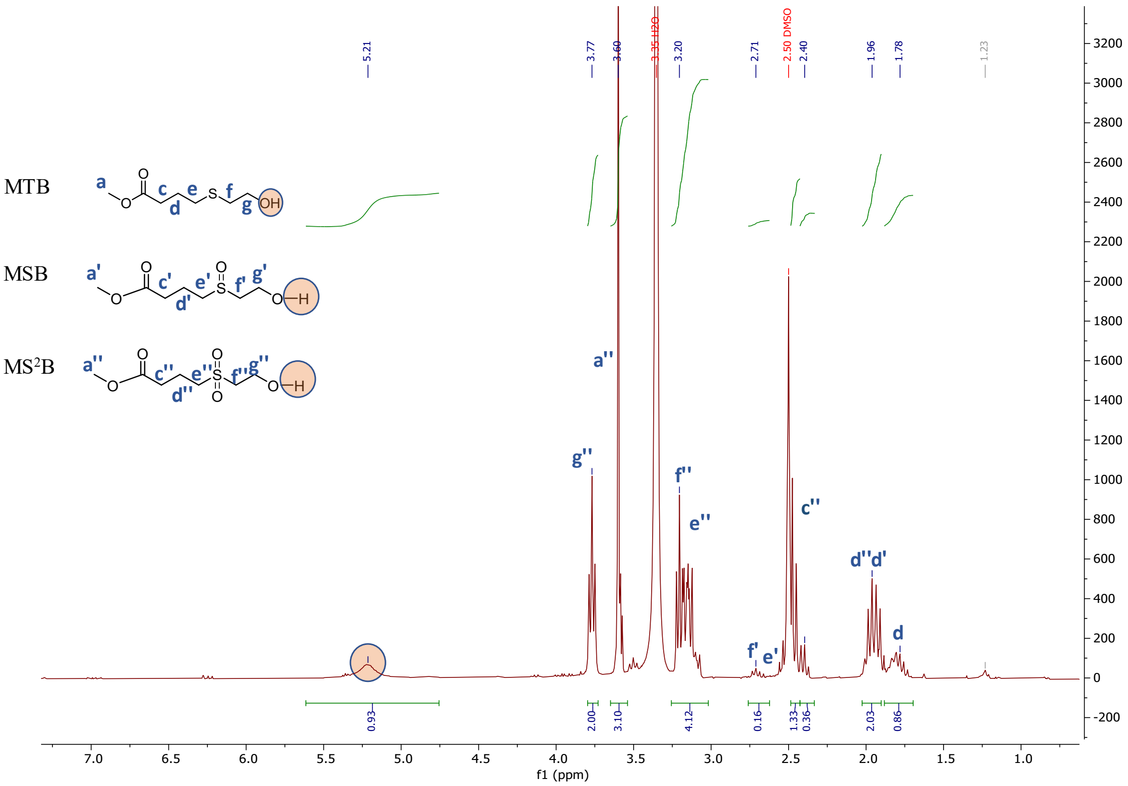


Figure S13. ^{1}H NMR spectrum of MTB oxidized by 20eq NaOCl before purification in DMSO-d6

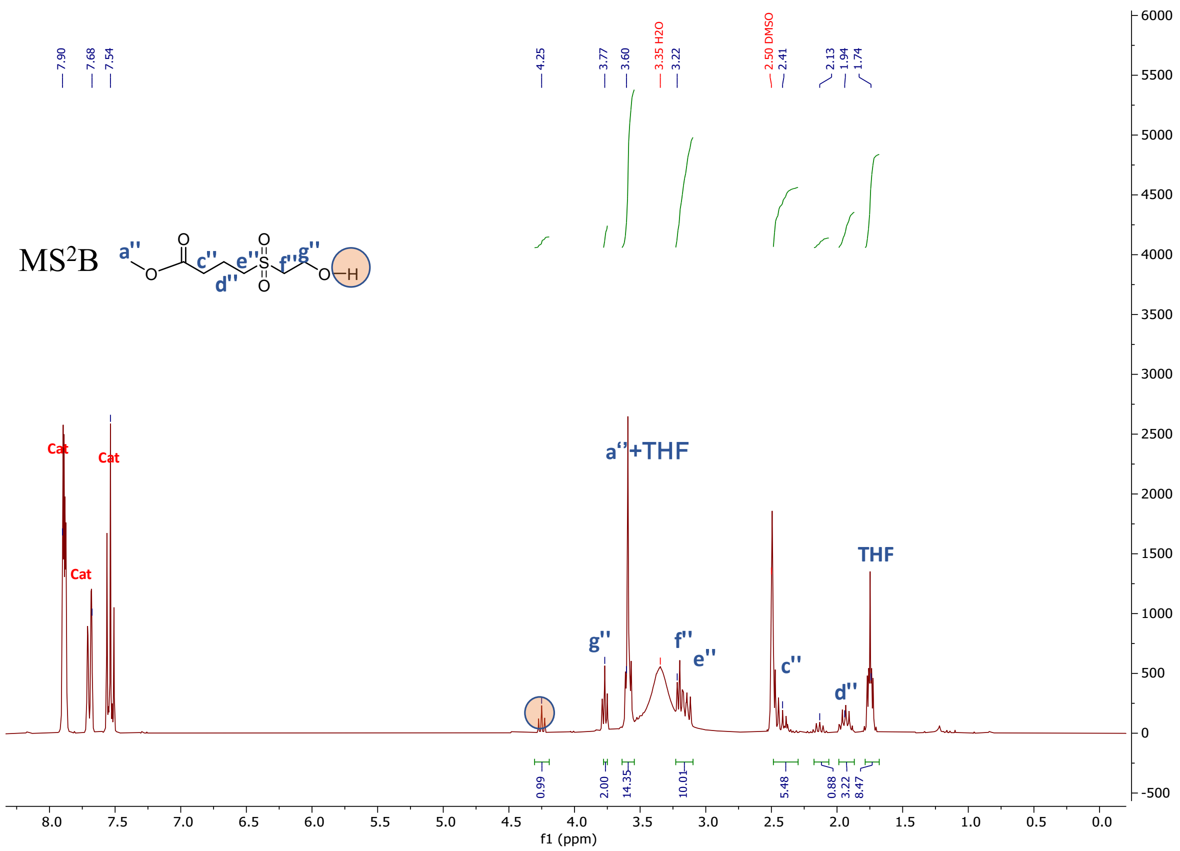


Figure S14. ^{1}H NMR spectrum of MTB oxidized by 20eq M-CPBA before purification in DMSO-d6

3.2. After purification

3.2.1. Sulfoxide

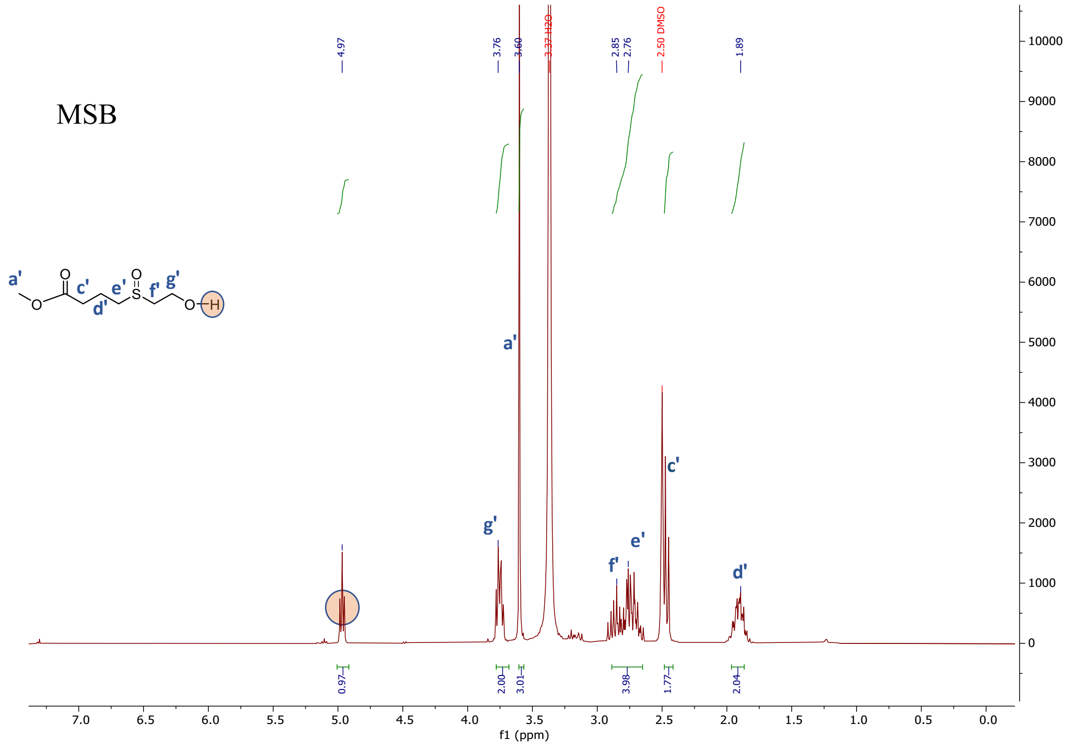


Figure S15. ^{1}H NMR spectrum of MTB oxidized by 2eq NaOCl after purification in DMSO-d6

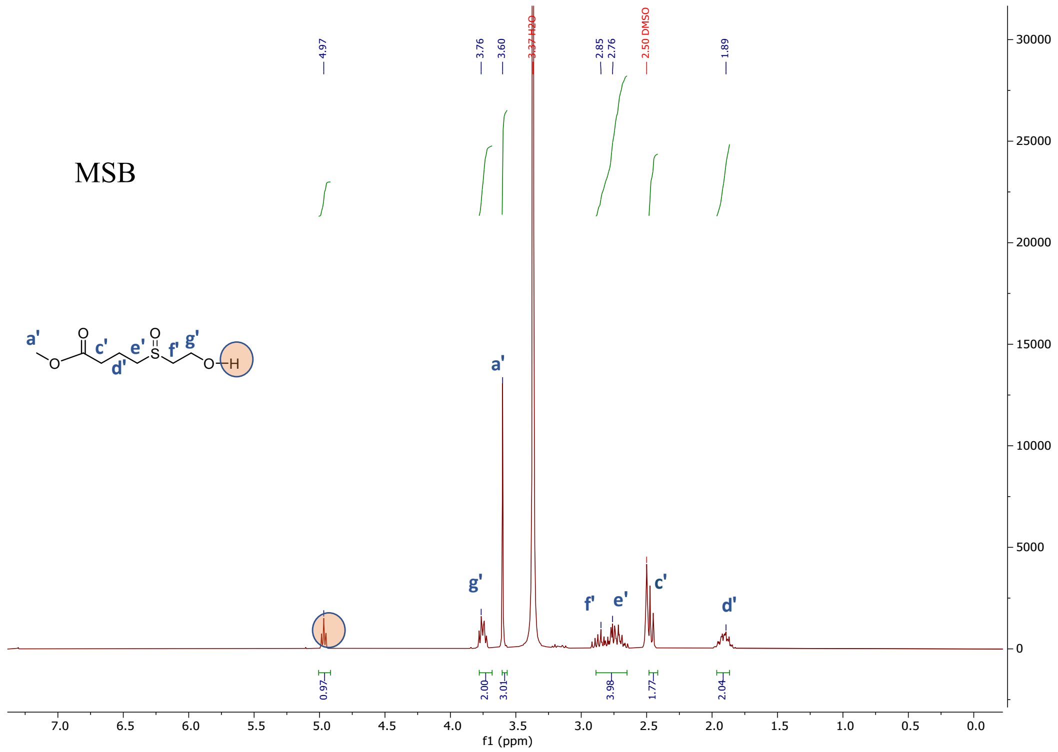


Figure S16. ^{1}H NMR spectrum of MTB oxidized by 2eq M-CPBA after purification in DMSO-d6

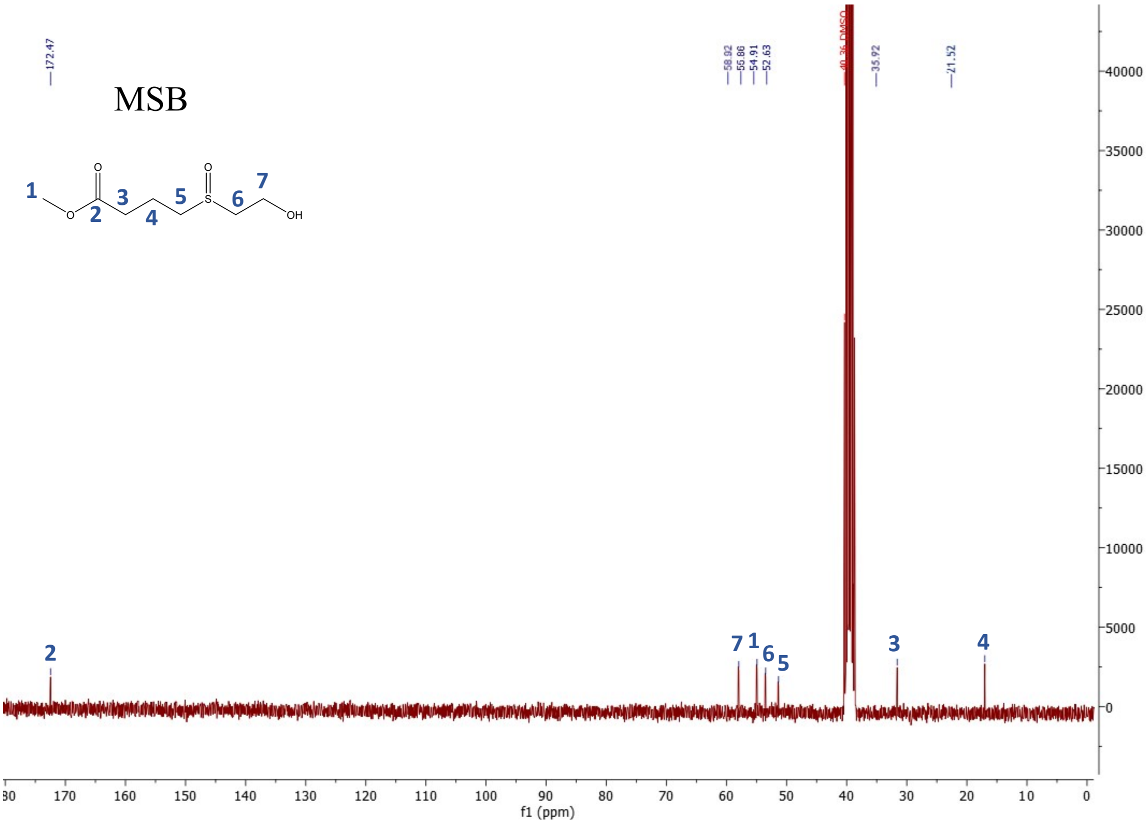


Figure S17. ^{13}C NMR spectrum of of MTB oxidized by 2eq NaOCl after purification in DMSO-d6

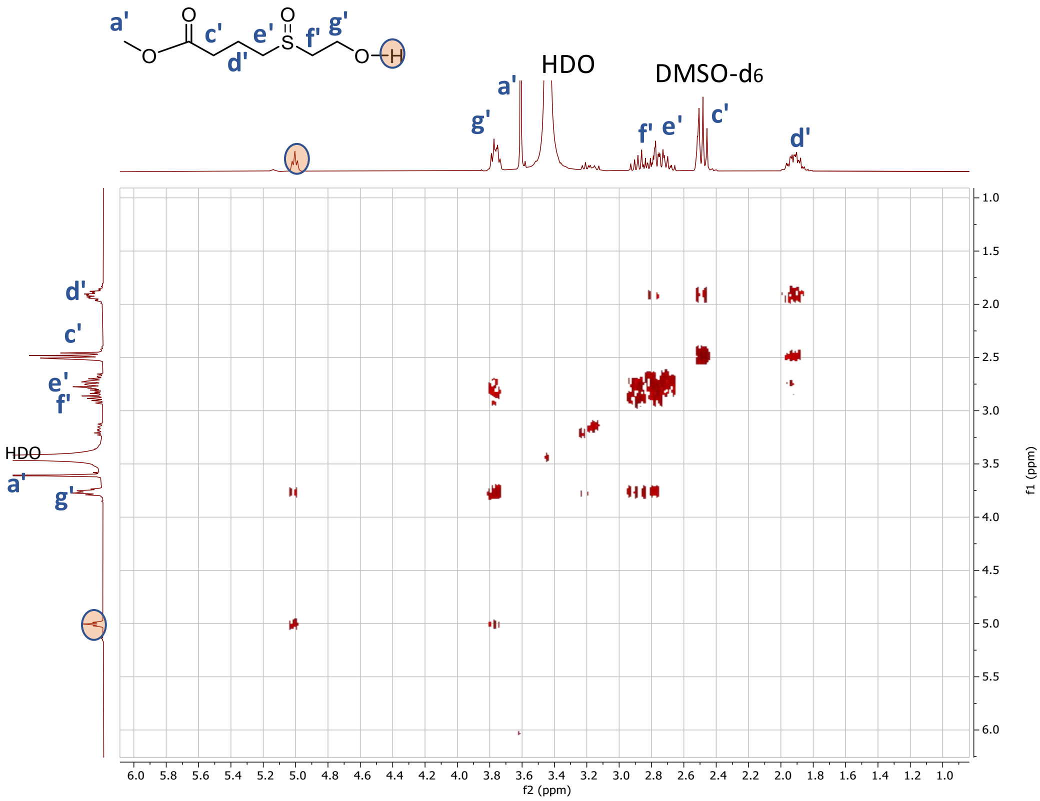


Figure S18. COSY spectrum of MTB oxidized by 2eq NaOCl after purification in DMSO-d6

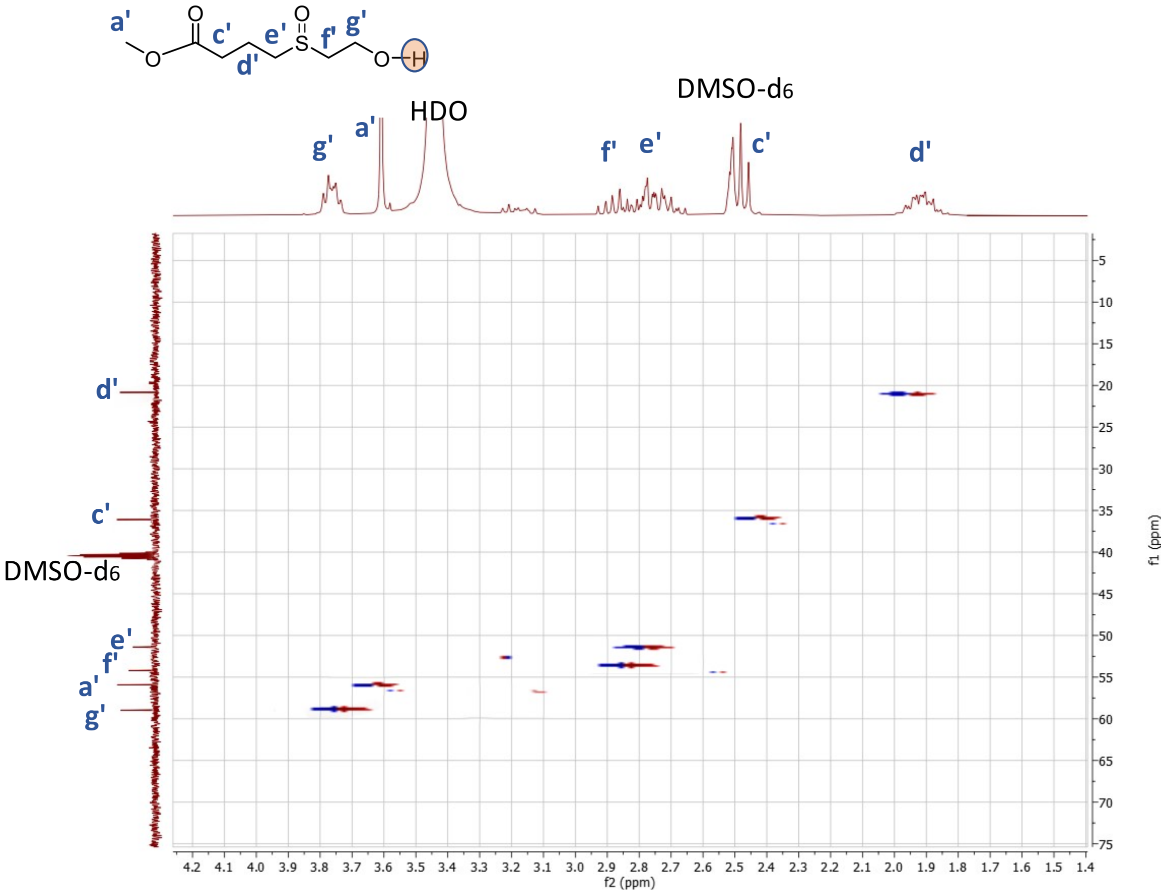


Figure S19. HSQC spectrum of of MTB oxidized by 2eq NaOCl after purification in DMSO-d6

3.2.2. Sulfone

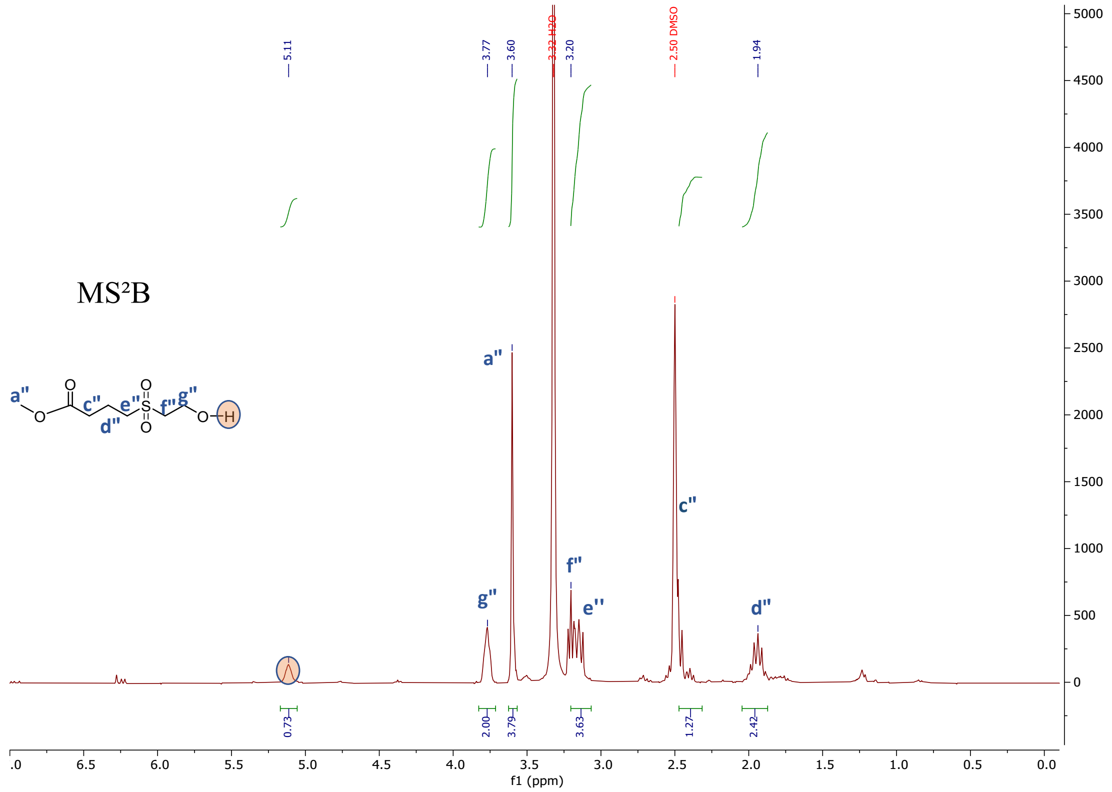


Figure S20. ^{1}H NMR spectrum of MTB oxidized by 20eq NaOCl after purification in DMSO-d6

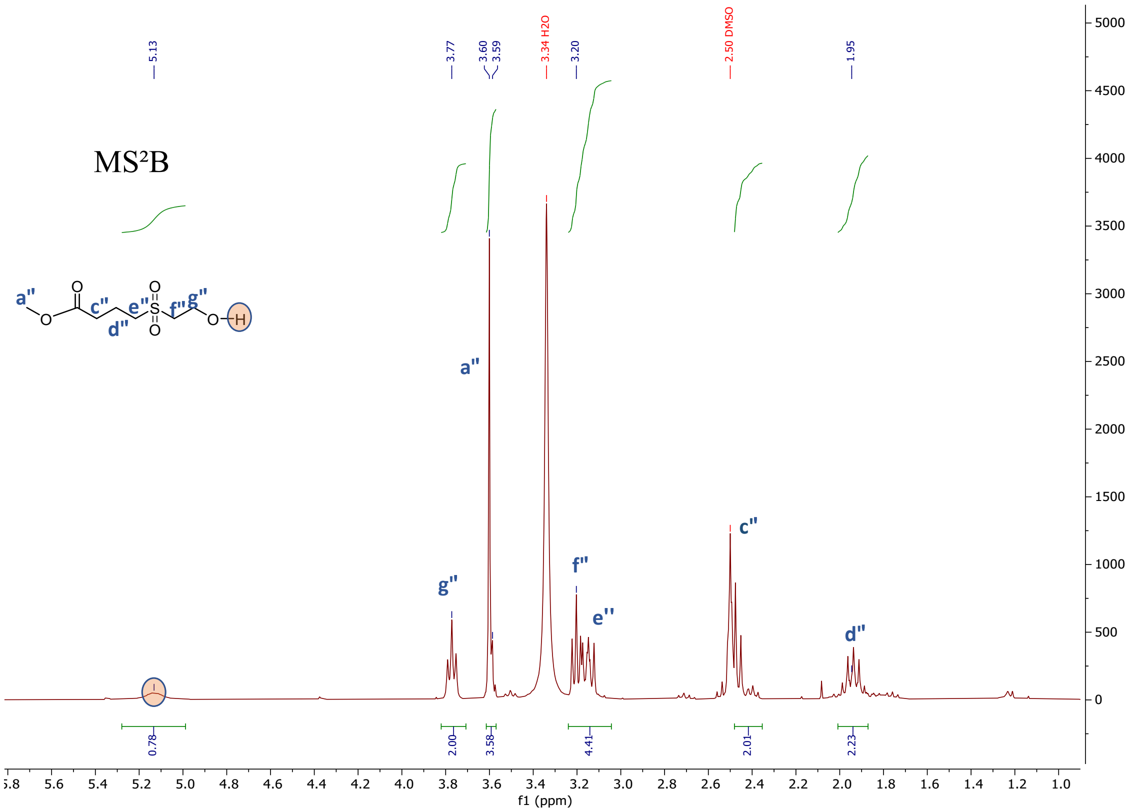


Figure S21. ^{1}H NMR spectrum of MTB oxidized by 20eq m-CPBA after purification in DMSO-d6

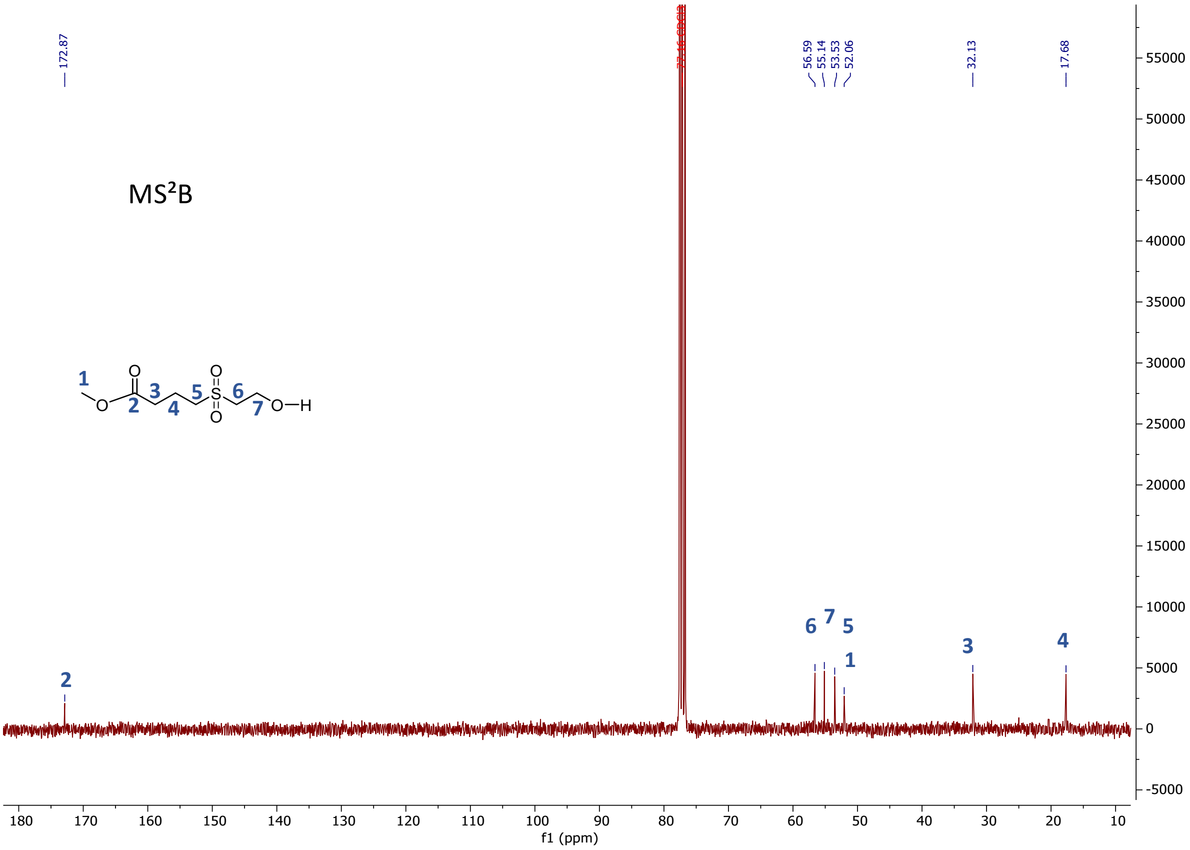


Figure S22. ^{13}C NMR spectrum of MS^{2}B oxidized by 20eq m-CPBA in $CDCl_3$

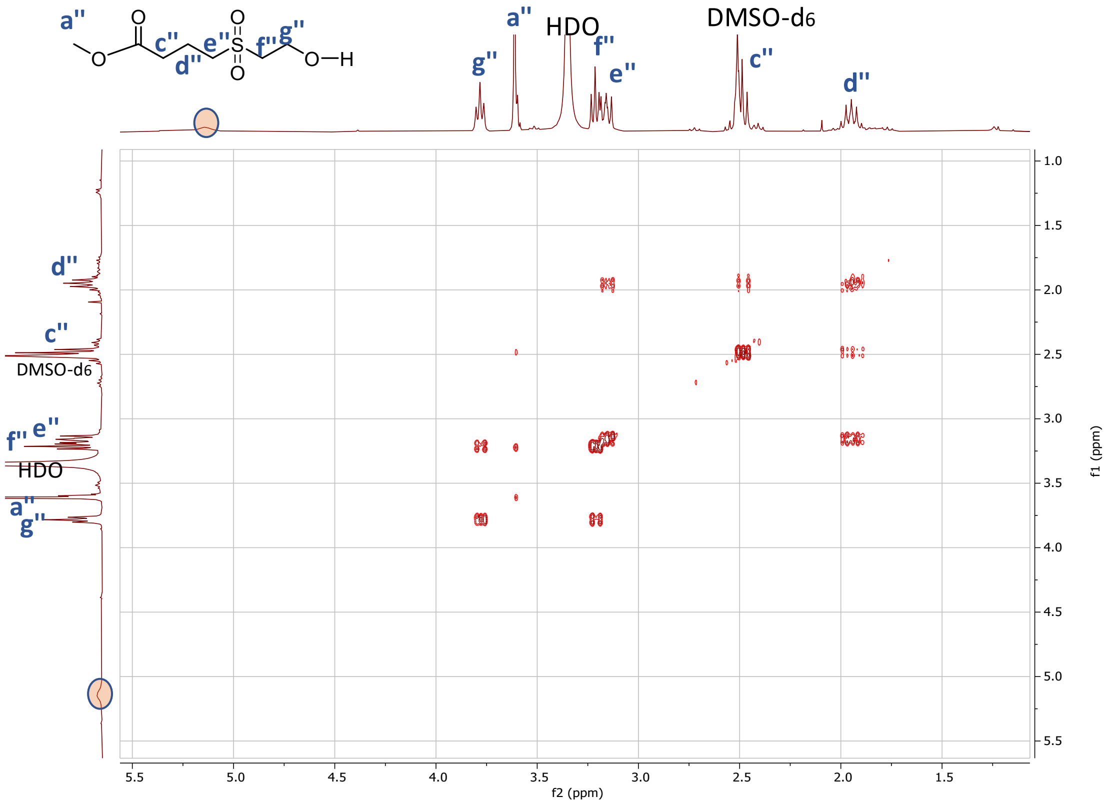


Figure S23. COSY spectrum of MS^{2}B oxidized by 20eq m-CPBA after purification in DMSO-d6

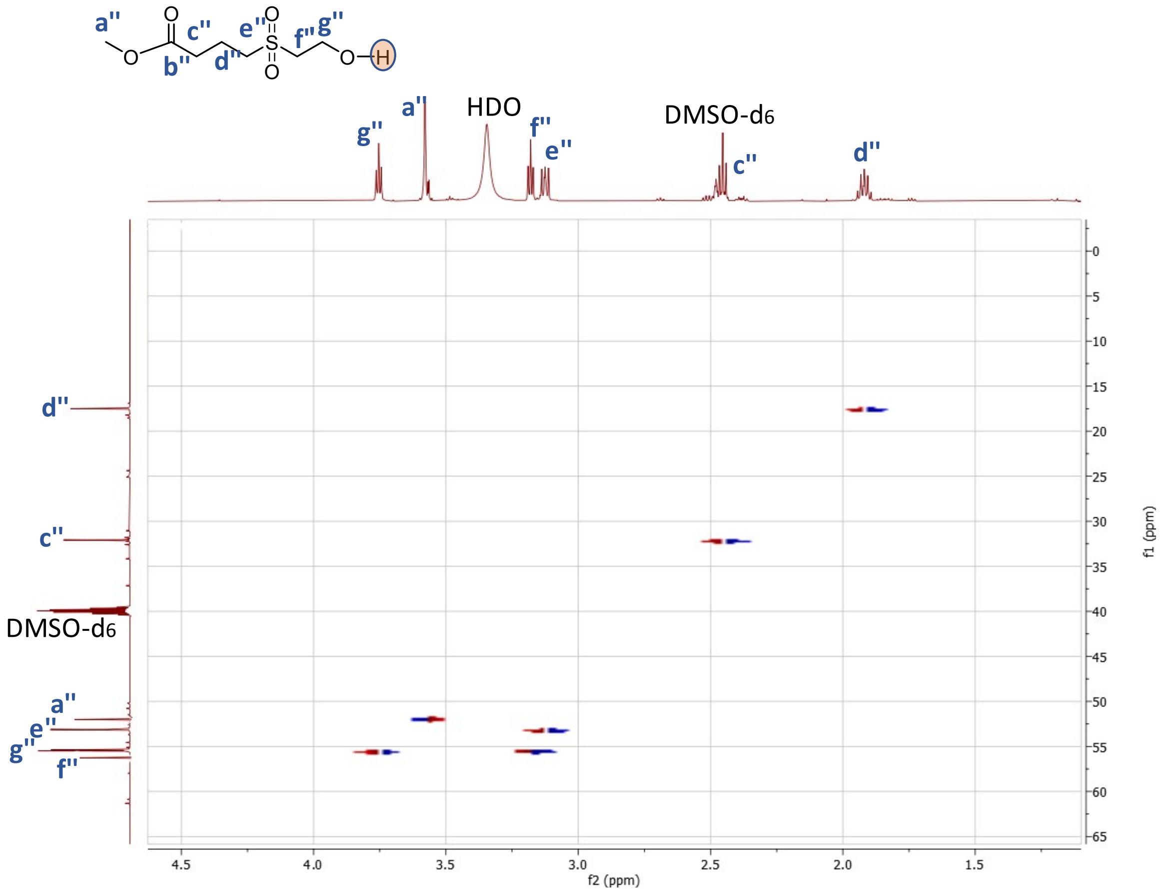
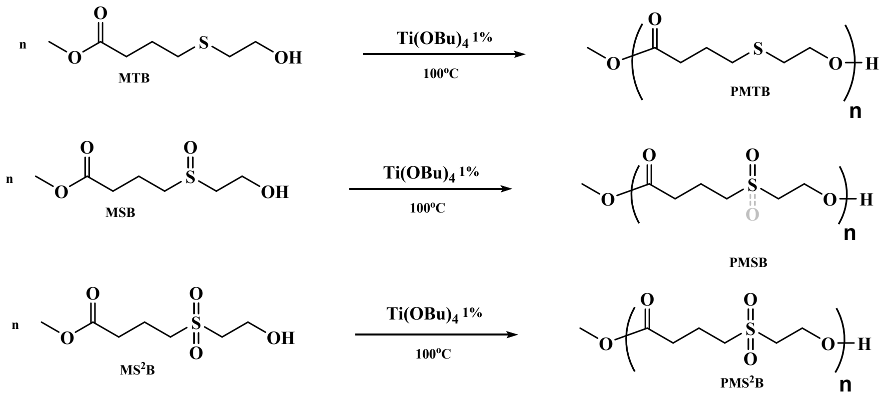


Figure S24. HSQC spectrum of MS^2B oxidized by 20eq m-CPBA after purification in DMSO-d6

4. Polycondensation



Scheme S2. Polycondensation of MTB, MSB, MS^2B

Figure S25. Experimental setup for polycondensation reactions

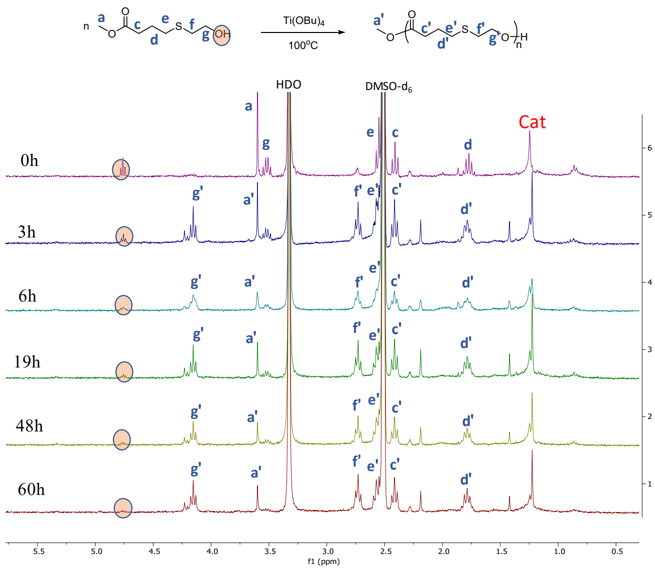


Figure S26. ^{1}H NMR spectrum of MTB polycondensation at 100°C (in DMSO-d_6)

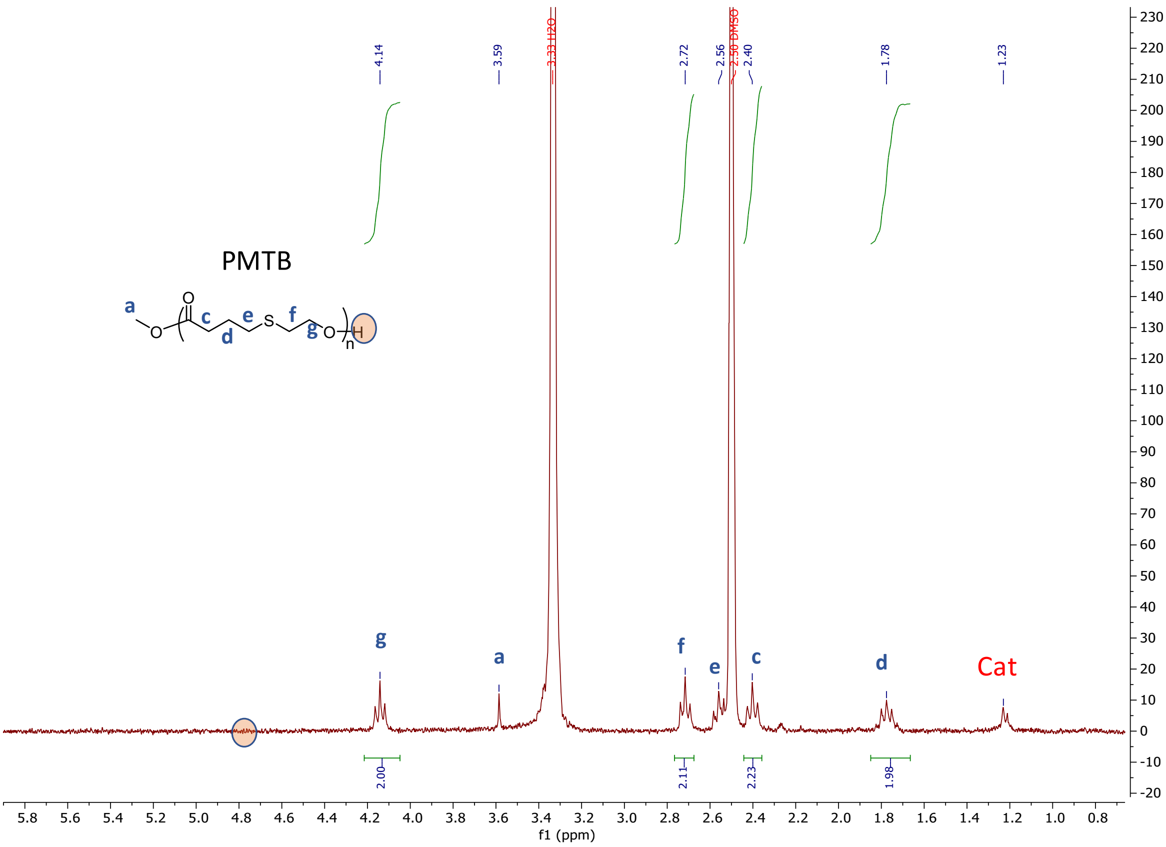


Figure S27. ^{1}H NMR spectrum of PMTB (in DMSO-d6)

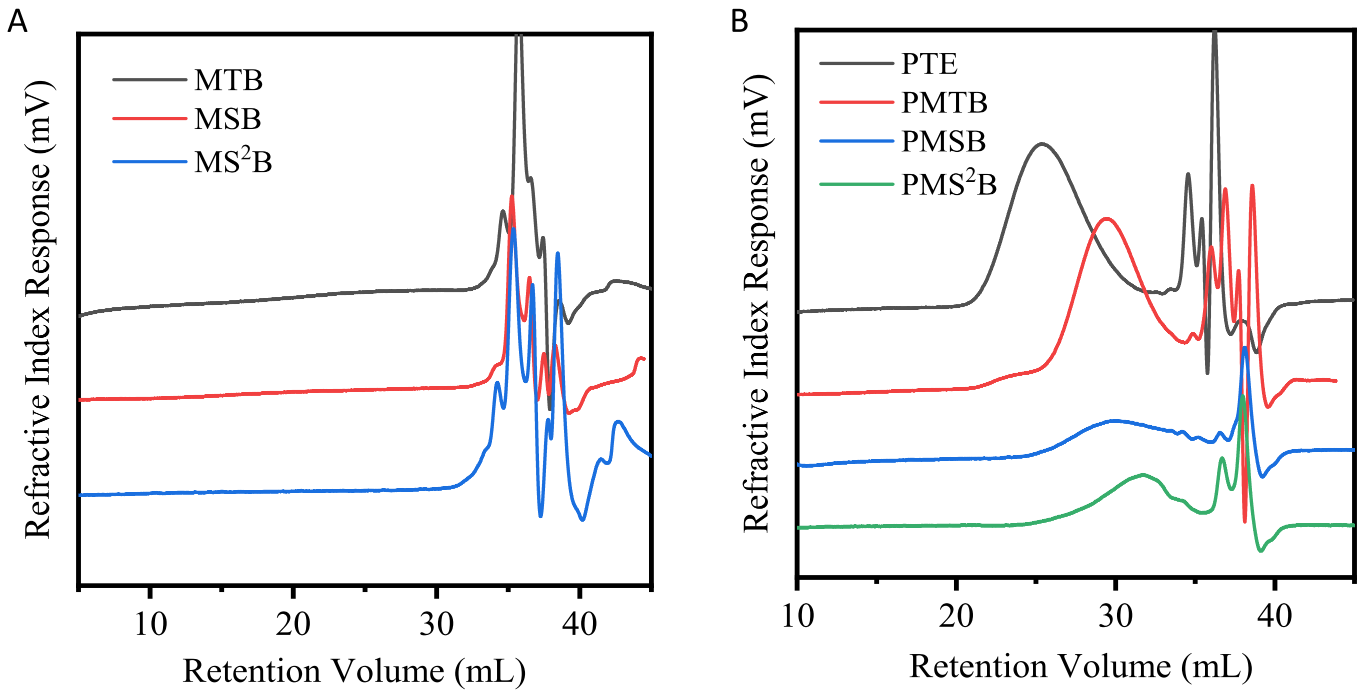


Figure S28. A SEC chromatograms comparison of MTB, MSB, MS^{2}B and **B** SEC chromatograms comparison of PTE, PMTB, PMSB, PMS^{2}B

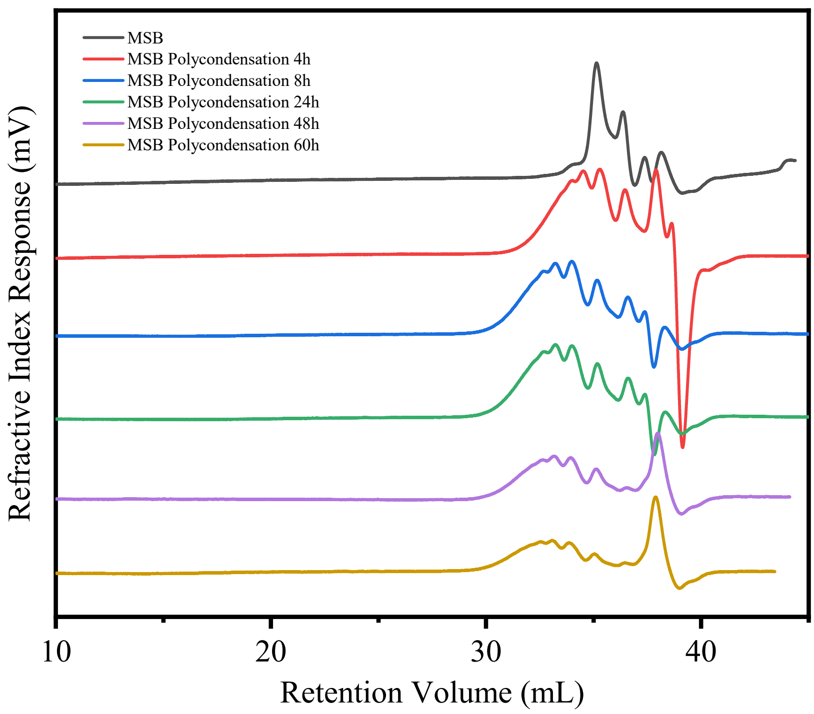


Figure S29. SEC chromatograms of MSB polycondensation over time

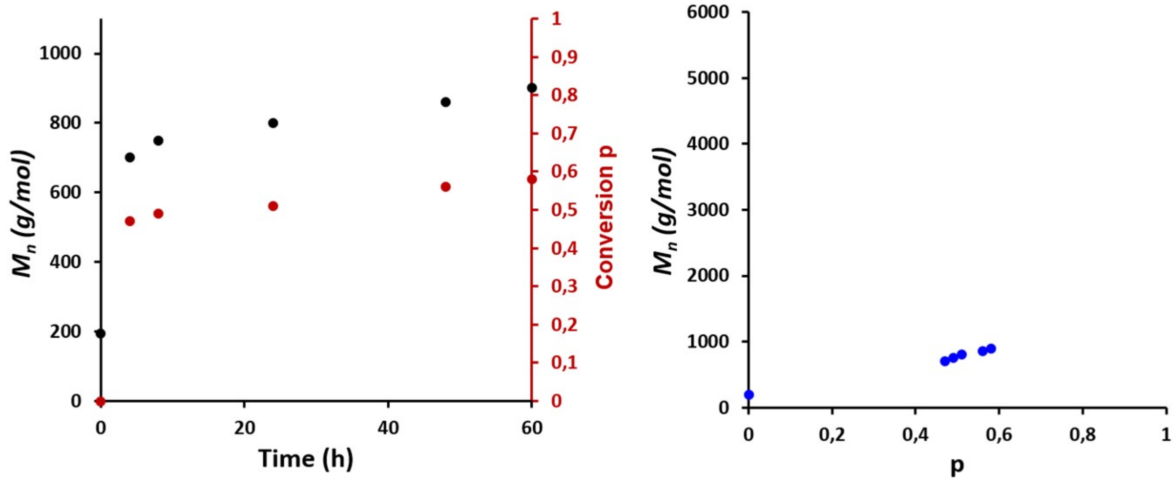


Figure S30. Evolution of polymerization kinetics of MSB showing the number-average molar mass M_n as functions of time (left) and conversion (right).

Table S3. Polycondensation of MTB, 1,6-Hexanediol and Adipic acid

Time (h)	$M_{n,\,SEC}$ after polycondensation (g mol⁻¹)	$M_{w,\,SEC}$ after polycondensation (g mol⁻¹)	Đ
3	260	348	1.3
24	828	1815	2.2
35	1751	2988	1.7
55	3210	7968	2.5
72	5650	16517	2.9

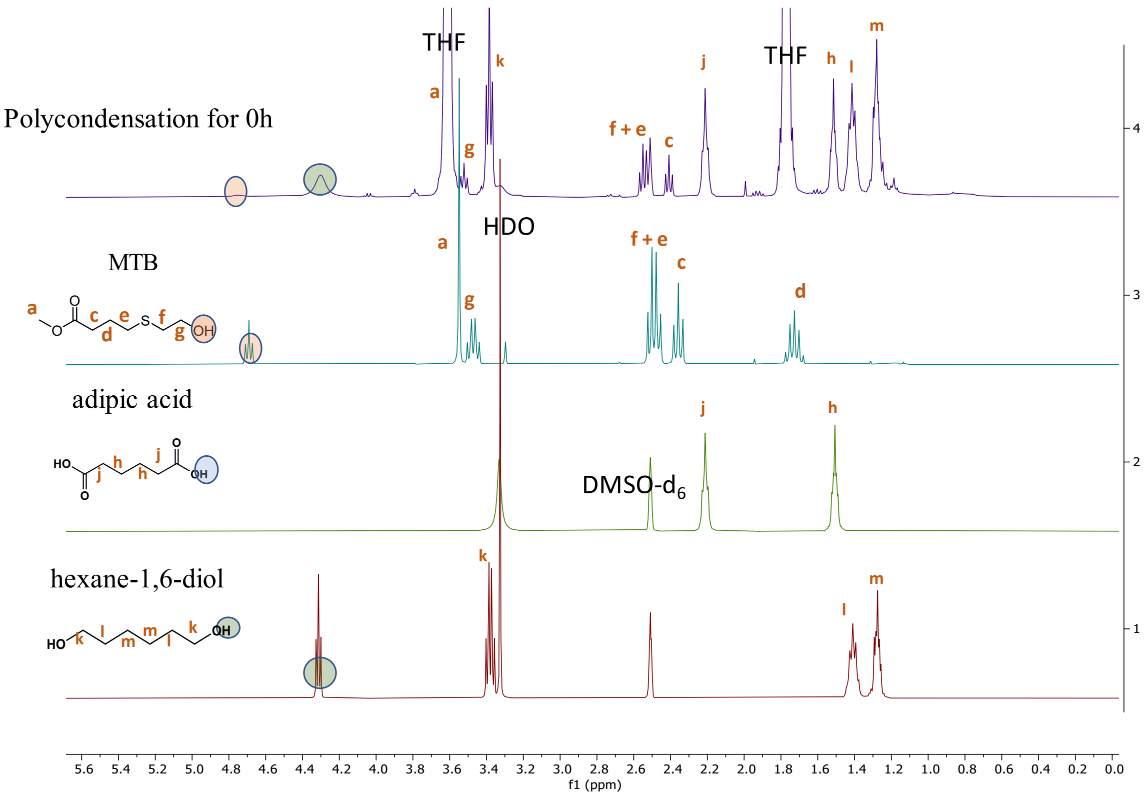


Figure S31. [1]H NMR spectra of hexane-1,6-diol, adipic acid, MTB monomers and of their mixture at t=0 (in DMSO-d_6)

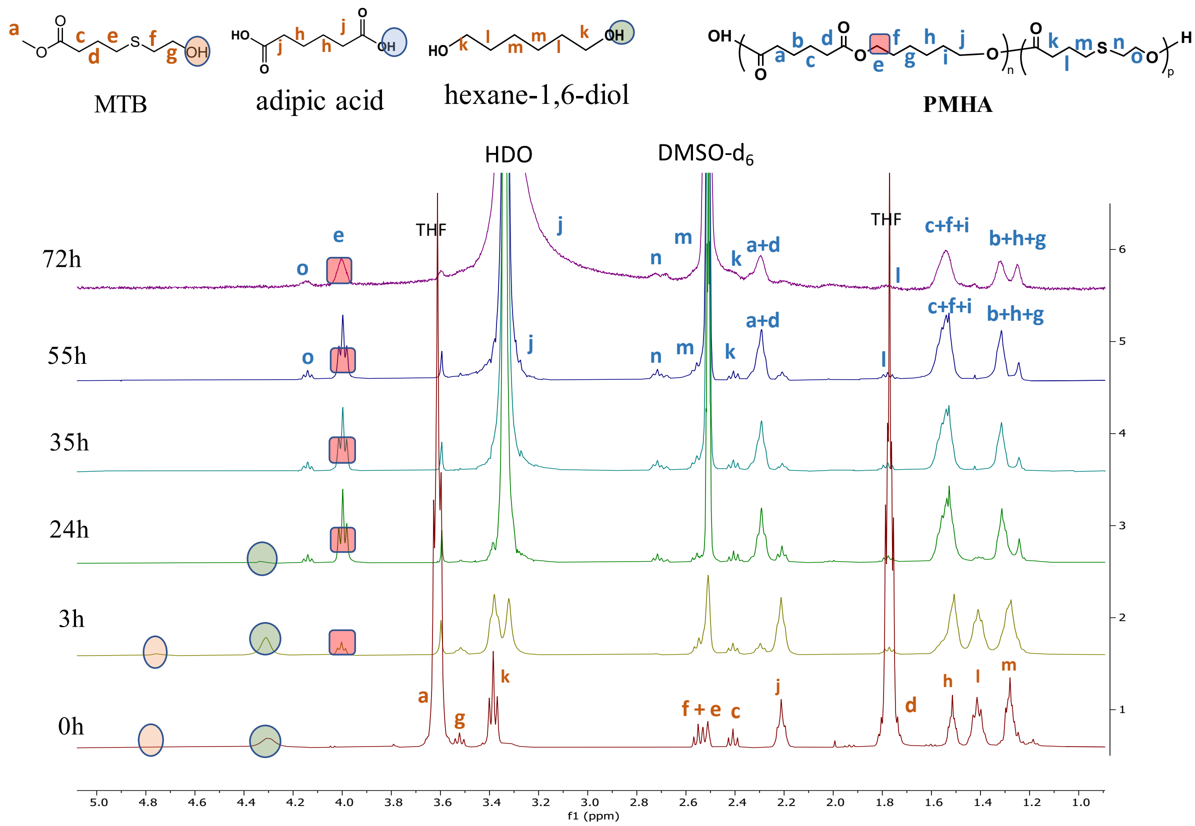


Figure S32. [1]H NMR spectrum of PMHA polycondensation reaction over time (in DMSO-d_6)

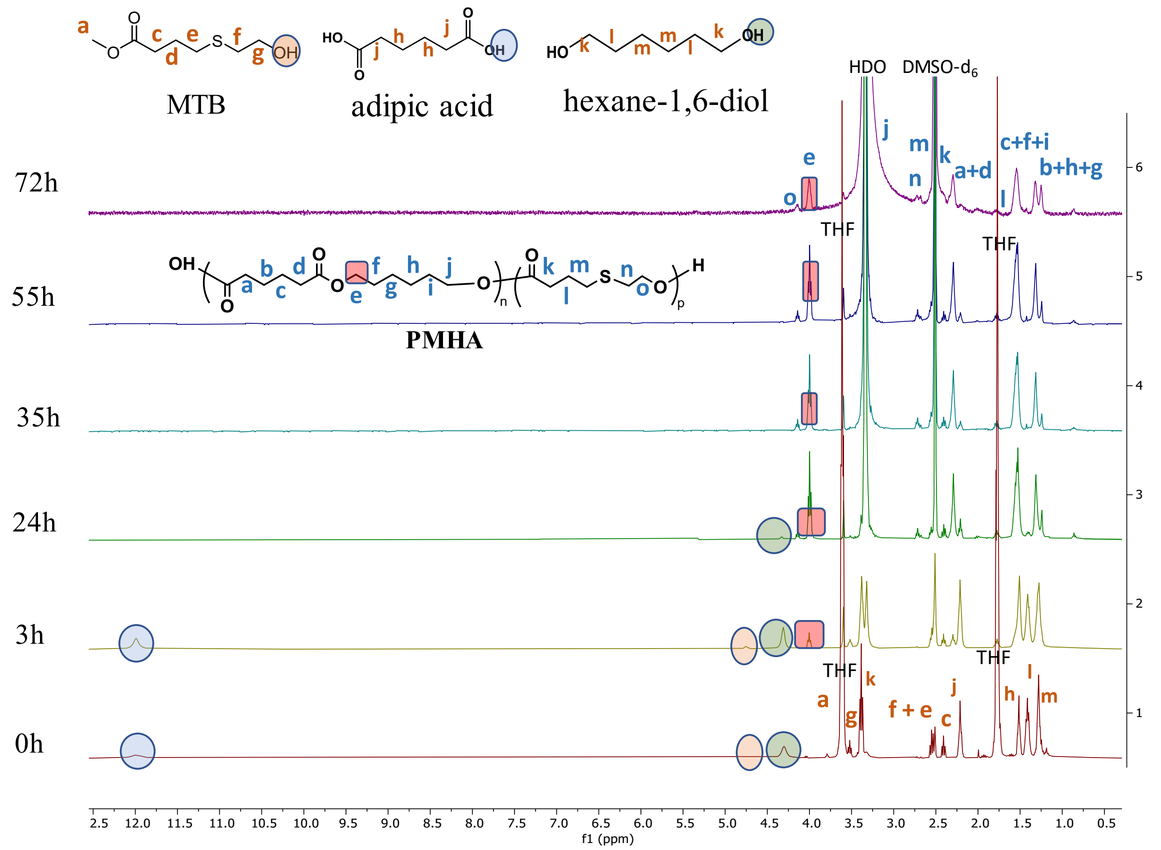


Figure S33. [1]H NMR spectrum of PMHA polycondensation reaction over time (in DMSO-d6)

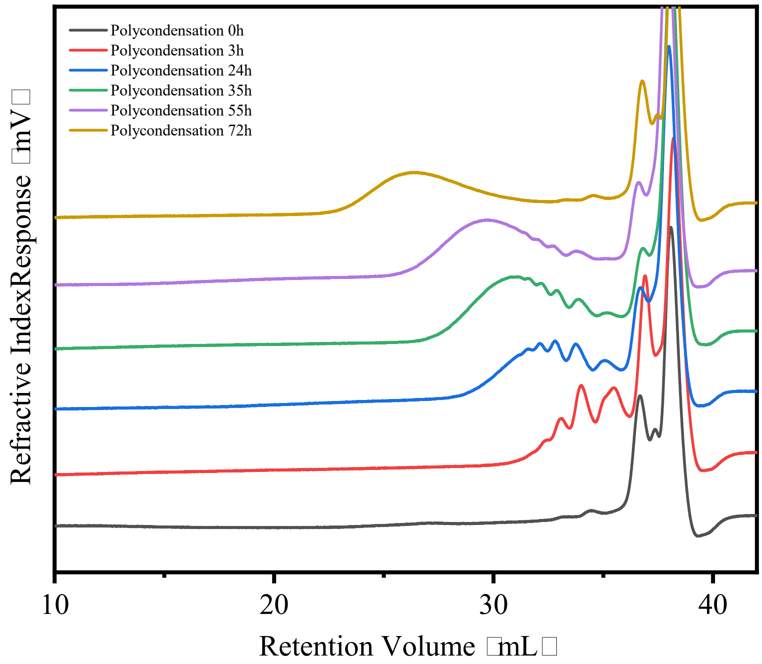


Figure S34. SEC chromatograms of PMHA polycondensation reaction over time

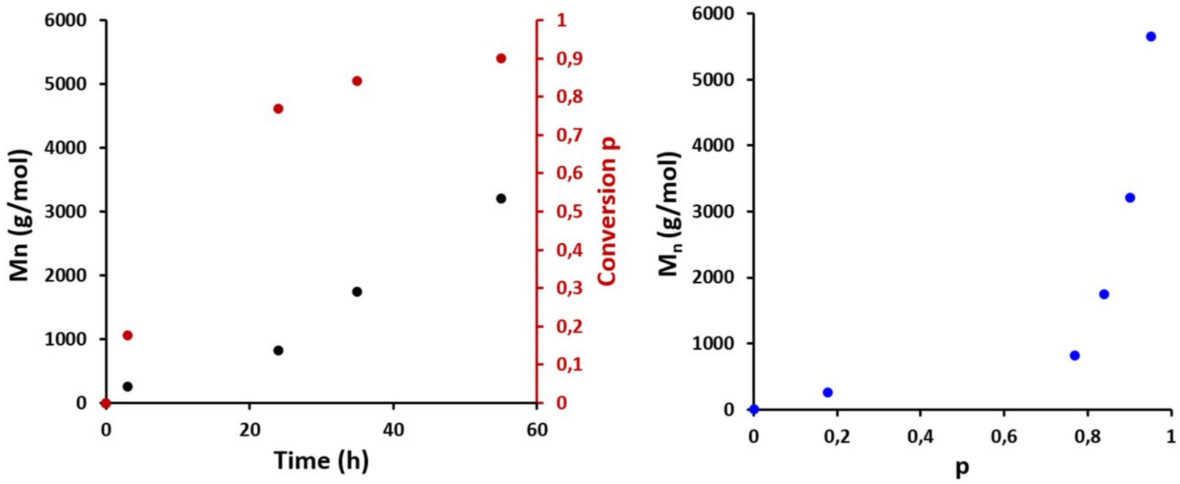


Figure S35. Evolution of polymerization kinetics of MTB, 1,6-hexanediol and adipic acid showing the number-average molar mass M_n as functions of time (left) and conversion (right).

5. TGA and DSC

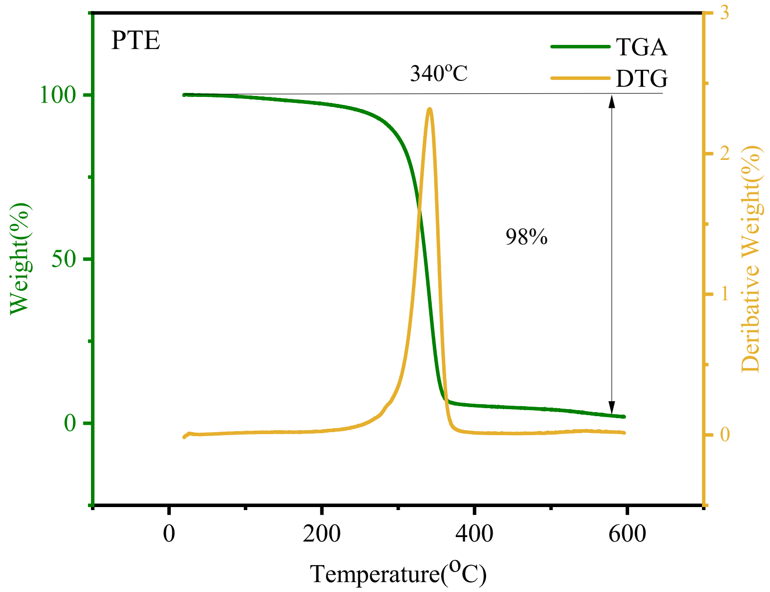


Figure S36. TGA curves of PTE 10°C/min

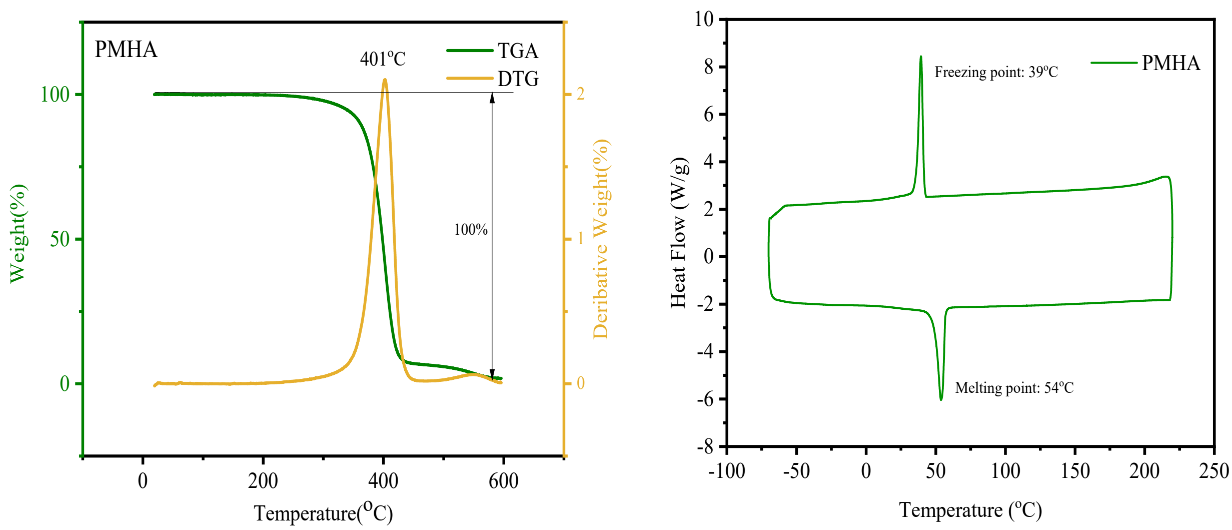


Figure S37. TGA and DSC curves of PMHA 10°C/min

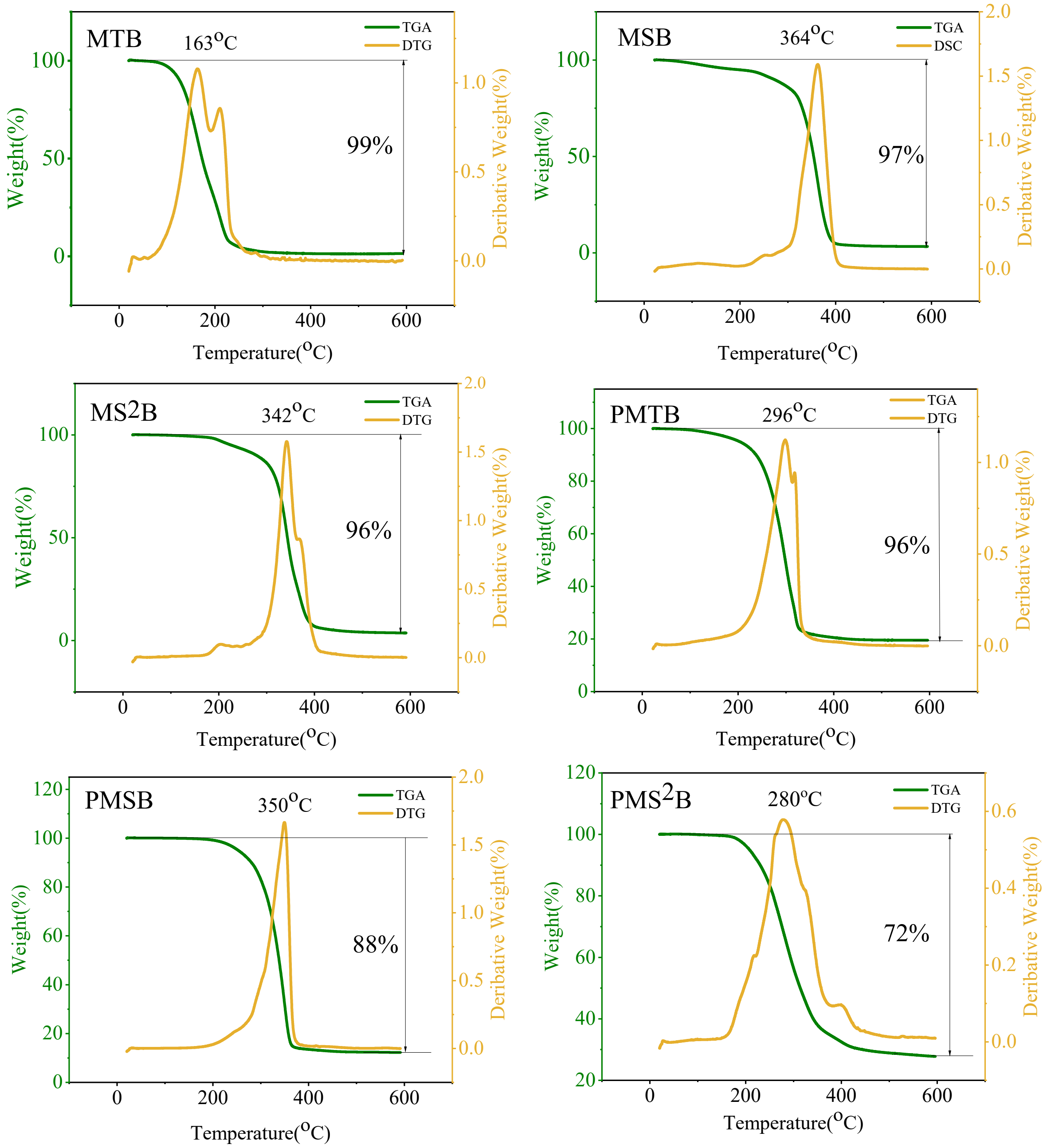


Figure S38. TGA curves of MTB MSB MS^{2}B, PTE, PMTB, PMSB and PMS^{2}B 10^{o}C/min

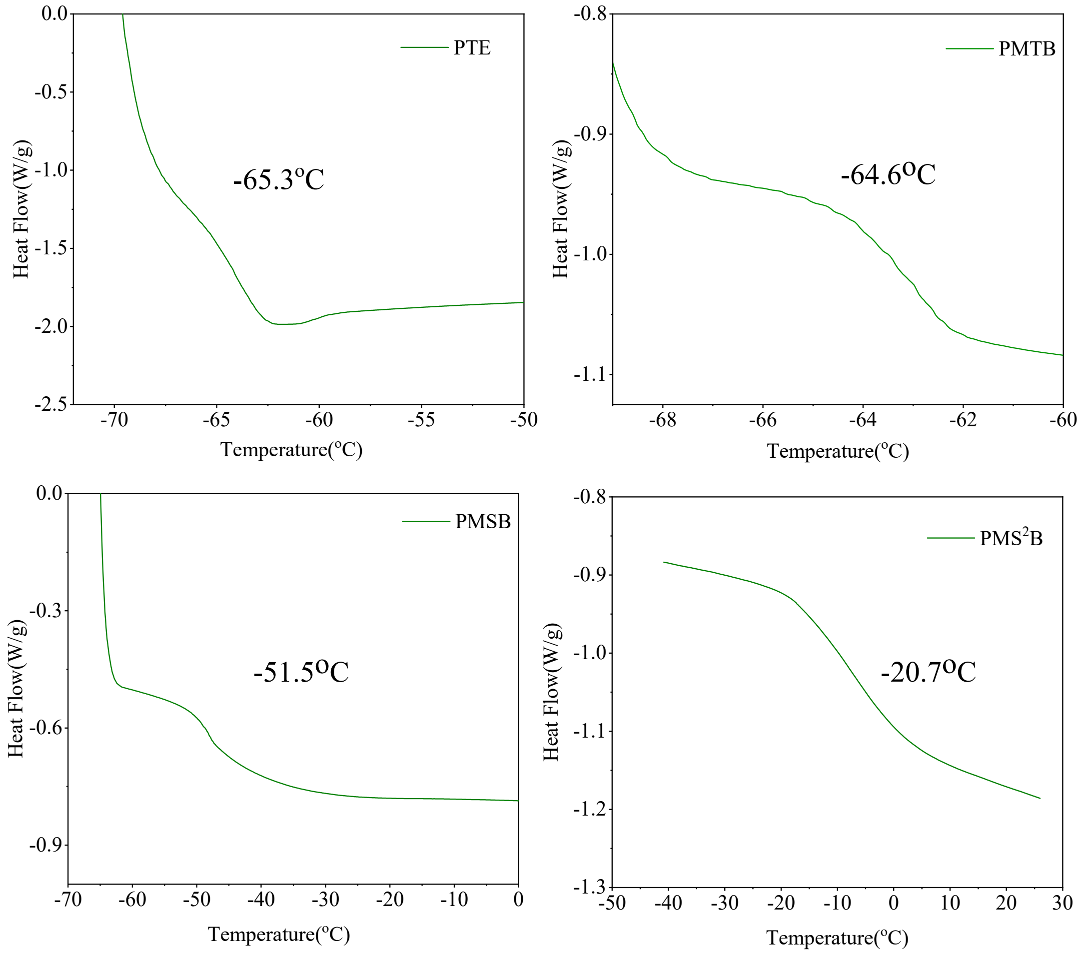


Figure S39. DSC curves of second heating scans at 10 °C min^{-1} of PTE, PMTB, PMSB and PMS^2B

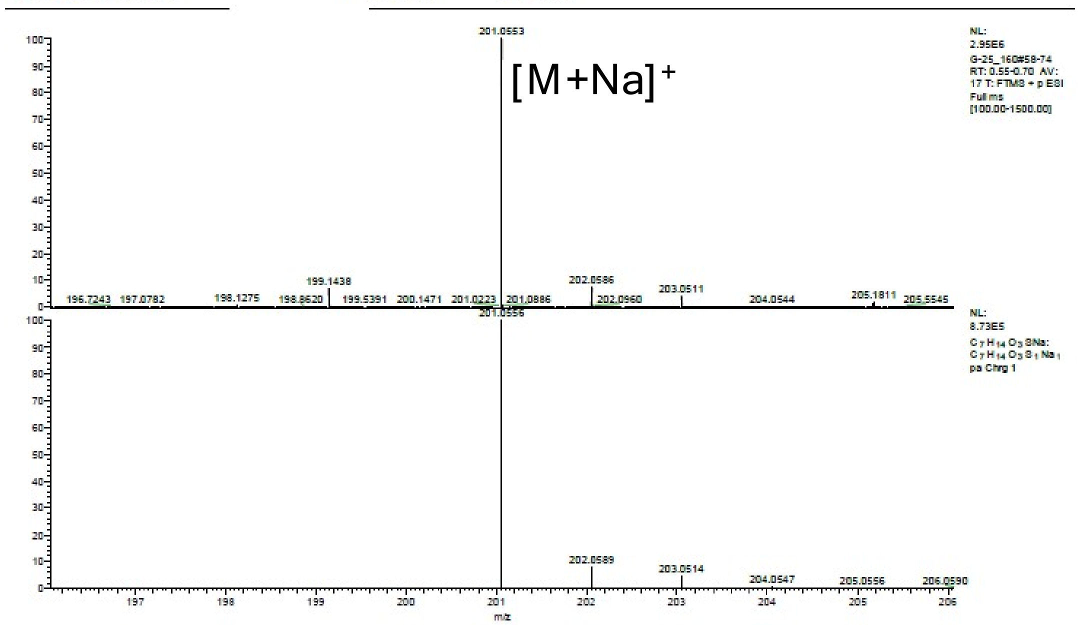
6. Monomer and Polymer Solubility Table

Table S4. Solubility of monomers and polymers in water

Run	Name	Solubility (√soluble, ×insoluble)
1	MTB	+
2	MSB	+
3	MS^2B	+
4	PTE	-
5	PMSB	-
6	PMS^2B	+/-

7. Individual HRMS results

M= MTB= $C_7H_{14}O_3SNa$



Experimental/theoretical isotopic pattern MS spectrum

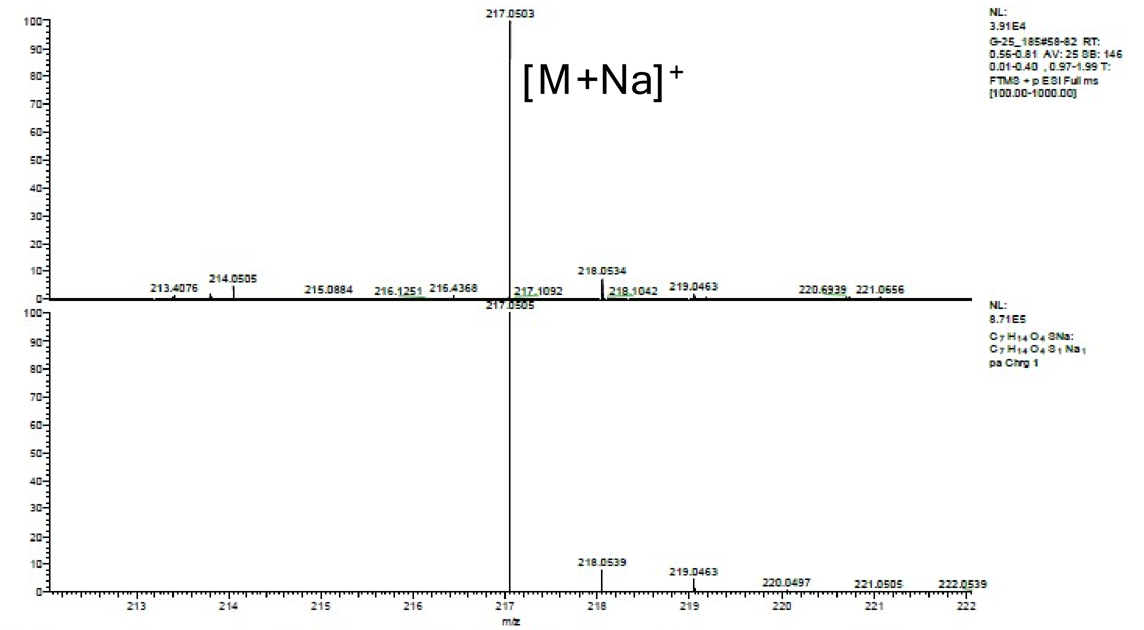
Error = -1.4 ppm; Relative Intensity (%) 100

HRMS (ESI) m/z: [M+Na]+ Calcd for C7H14O3SNa 201.0556. Found 201.0553; (Error: -1.4 ppm).

COMPLIANT

Figure S40. HRMS analysis of MTB

M= MSB= $C_7H_{14}O_4SNa$



Experimental/theoretical isotopic pattern MS spectrum

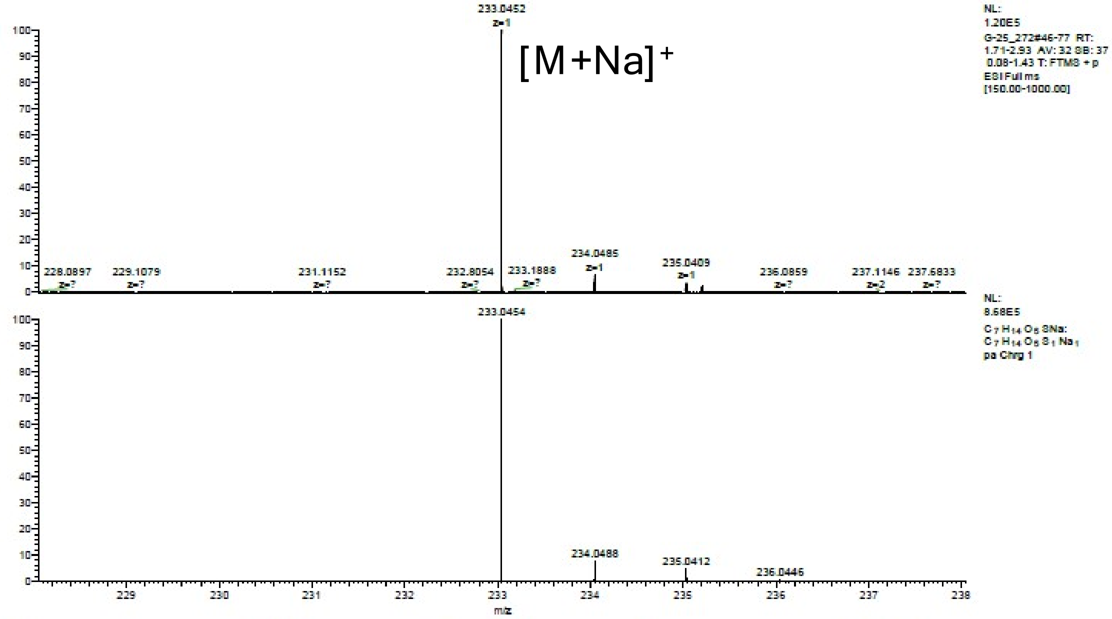
Error = -0.9 ppm; Relative Intensity (%) 100

HRMS (ESI) m/z: [M+Na]+ Calcd for C7H14O4SNa 217.0505. Found 217.0503; (Error: -0.9 ppm).

COMPLIANT

Figure S41. HRMS analysis of MSB

M= MS^2B= $C_7H_{14}O_5SNa$



Experimental/theoretical isotopic pattern MS spectrum

Error = -0.9 ppm; Relative Intensity (%) 100

HRMS (ESI) m/z: [M+Na]+ Calcd for C7H14O5SNa 233.0454. Found 233.0452; (Error: -0.9 ppm).

COMPLIANT

Figure S42. HRMS analysis of MS^2B