Electronic Supplementary Material (ESI) for Journal of Materials Chemistry B.

Electronic Supplementary Information

Biodegradable crosslinked polyesters derived from thiomalic acid and *S*-nitrosothiol analogues for nitric oxide release

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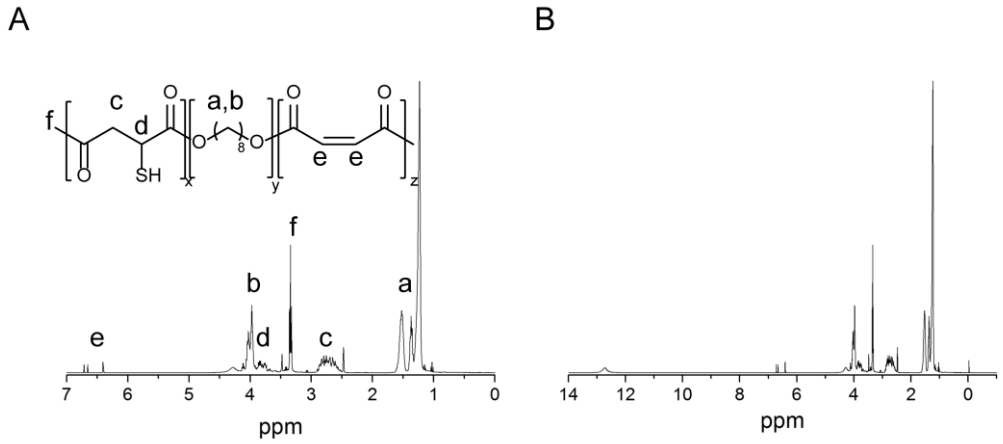


Figure S1. Selected portion (A) and complete ^{1}H NMR spectrum of PTMO (B). ^{1}H NMR δ_H/ppm (400 MHz, DMSO-d_6): 12.73 (–CO_2H), 6.67–6.73 (–HC=CH–), 3.94–4.07 (–OCH_2–), 3.72–3.89 (–S–CH–CO_2–), 3.32–3.35 (–CH_2OH), 2.58–2.91 (–CH_2CO_2–), 2.49 (DMSO), 1.52–1.60 (–CH_2–$(CH_2)_4$–CH_2–),1.34–1.39 (–CH_2–CH_2OH), 1.24 (–$(CH_2)_4$–).

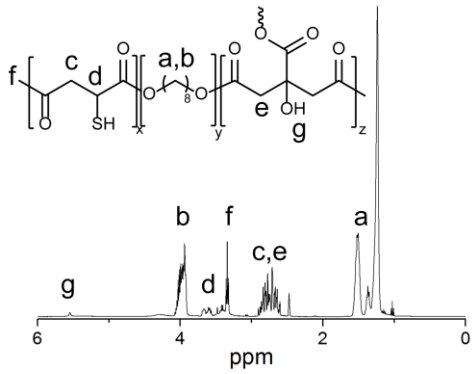


Figure S2. ^{1}H NMR spectrum of PTCO. ^{1}H NMR δ_H/ppm (400 MHz, DMSO-d_6): 5.56 (–C–OH), 3.93–4.07 (–OCH_2–), 3.58–3.69 (–S–CH–CO_2), 3.32–3.36 (–CH_2OH), 2.61–2.91 (–CH_2CO_2–), 2.49 (DMSO), 1.51–1.53 (–CH_2–$(CH_2)_4$–CH_2–), 1.36–1.39 (–CH_2–CH_2OH), 1.25 (–$(CH_2)_4$–).

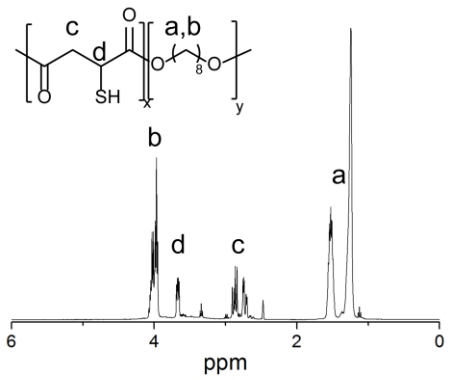


Figure S3. ^{1}H NMR spectrum of PTO. ^{1}H NMR δ_H/ppm (400 MHz, DMSO-d_6): 3.94–4.06 (–OC*H*$_2$–), 3.66–3.70 (–S–C*H*–CO$_2$–), 2.71–2.91 (–C*H*$_2$CO$_2$–), 2.49 (DMSO), 1.57 (–C*H*$_2$–(CH$_2$)$_4$–C*H*$_2$–), 1.25–1.30 (–(C*H*$_2$)$_4$–).

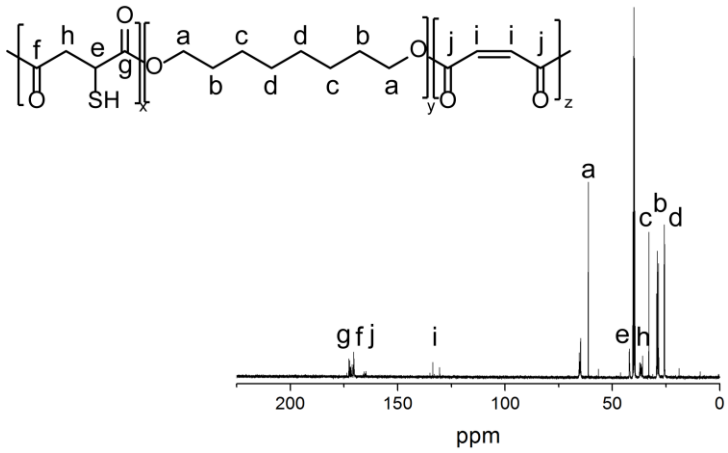


Figure S4. ^{13}C NMR spectrum of PTMO. ^{13}C NMR δ_C/ppm (100 MHz, DMSO–d_6): 170.3–172.6 (–*C*O$_2$–), 130.4–133.6 (–H*C*=*C*H–),64.8–65.5 (–*C*H$_2$OH), 61.2 (–OCH$_2$–), 41.9–42.0 (–S–*C*H–CO$_2$–), 39.3–40.6 (DMSO), 35.9–37.1 (–*C*H$_2$CO$_2$–), 33.0 (–*C*H$_2$–CH$_2$OH), 29.0–29.3 (–(*C*H$_2$)$_2$–), 28.4–28.5 (–*C*H$_2$–(CH$_2$)$_4$–*C*H$_2$–), 25.7–25.9 (–(*C*H$_2$)$_2$–).

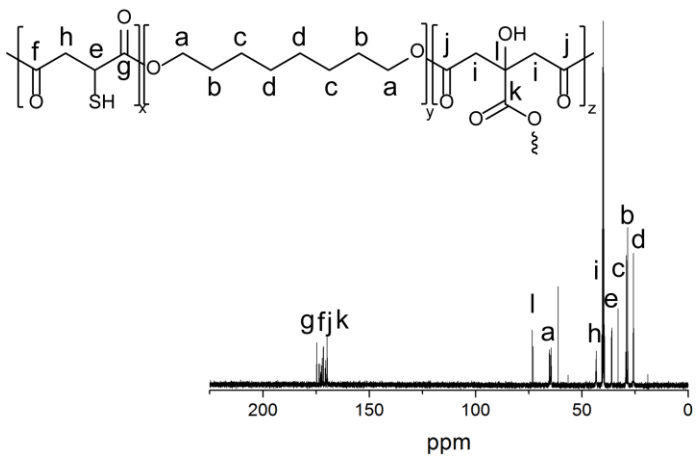


Figure S5. ^{13}C NMR spectrum of PTCO. ^{13}C NMR δ_C/ppm (100 MHz, DMSO–d_6): 169.6–174.9 (–*C*O_2–), 72.9–73.3 (–*C*–OH), 64.4–65.3 (–O*C*H_2–), 61.2 (–*C*H_2OH), 41.9–42.0 (–*C*$H_2C O_2$–), 39.3–40.6 (DMSO), 35.8–35.9 (–S–*C*H–CO_2–), 33.0 (–(*C*H_2)$_2$–), 28.4–28.5 (–*C*H_2–(CH_2)$_4$–*C*H_2–), 25.6–25.9 (–(*C*H_2)$_2$–).

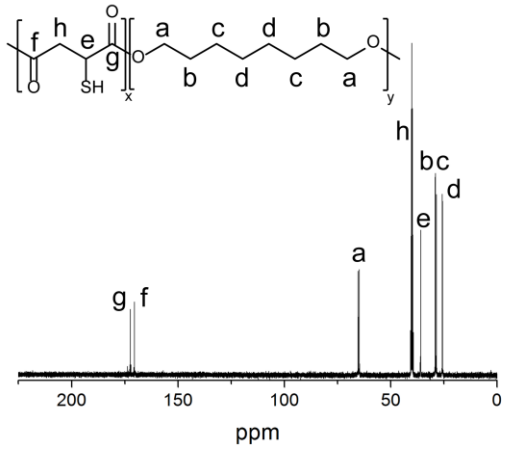


Figure S6. ^{13}C NMR spectrum of PTO. ^{13}C NMR δ_C/ppm (100 MHz, DMSO–d_6): 170.4–173.7 (–*C*O_2–), 64.7–65.2 (–O*C*H_2–), 39.3–40.6 (DMSO), 39.8 (–*C*$H_2C O_2$–), 35.9–36.1 (–S–*C*H–CO_2–), 29.0 (–*C*H_2–(CH_2)$_4$–*C*H_2–), 28.4–28.5 (–(*C*H_2)$_2$–), 25.6–25.7 (–(*C*H_2)$_2$–).

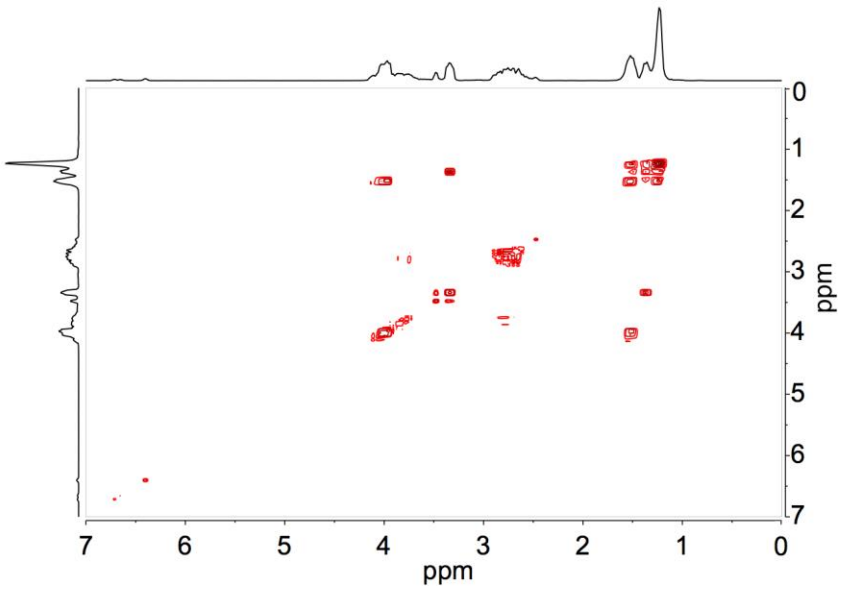


Figure S7. COSY 2D NMR spectrum of PTMO.

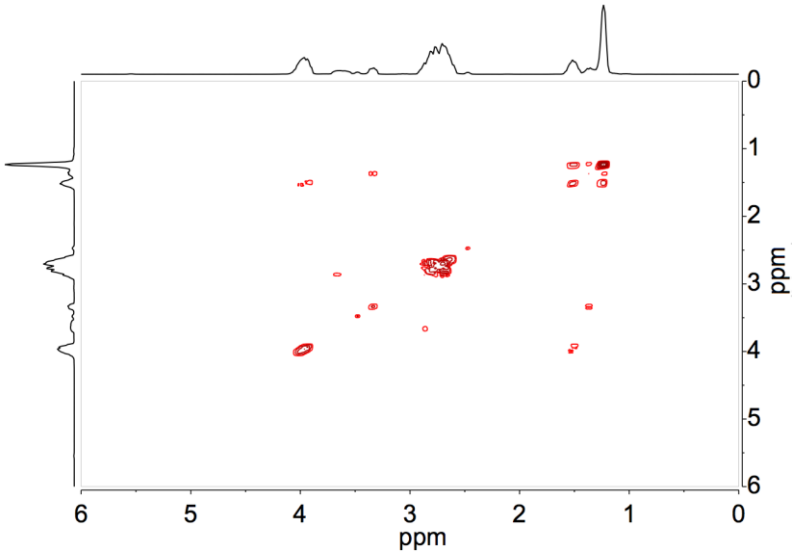


Figure S8. COSY 2D NMR spectrum of PTCO.

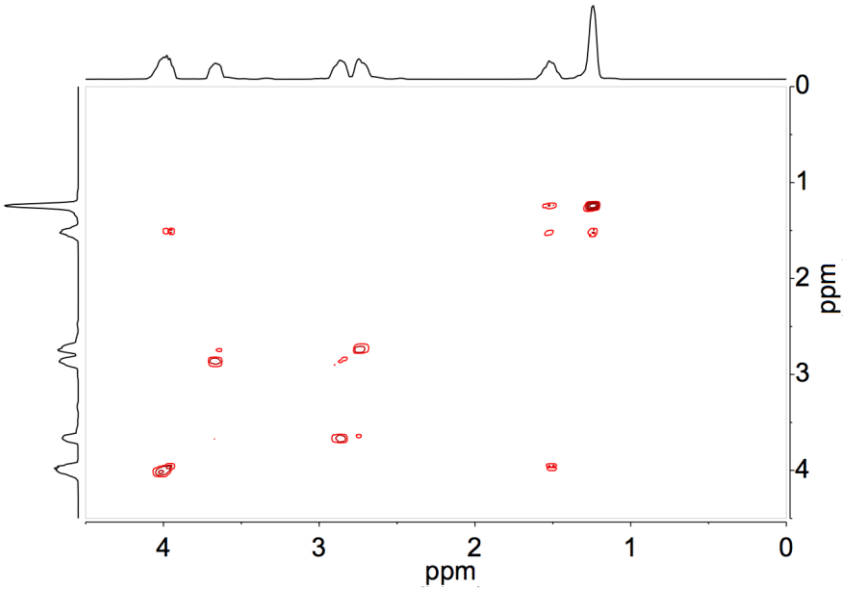


Figure S9. COSY 2D NMR spectrum of PTO.

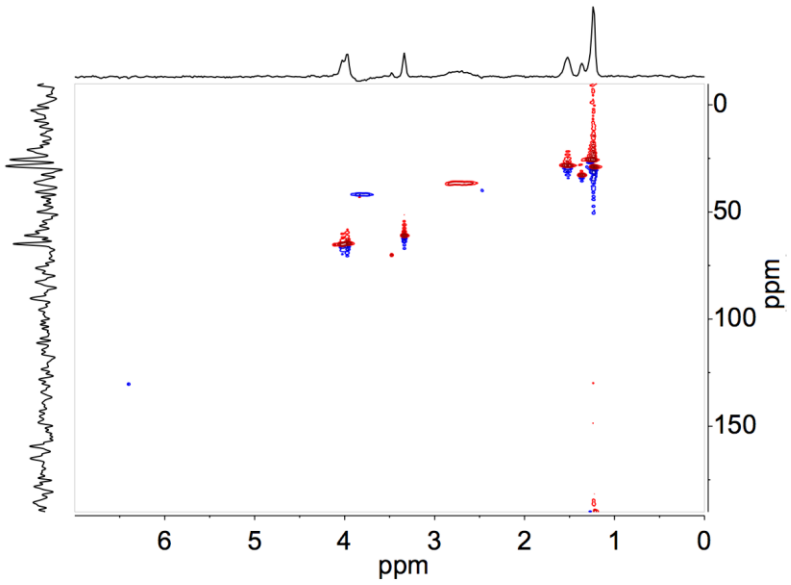


Figure S10. HSQC 2D NMR spectrum of PTMO.

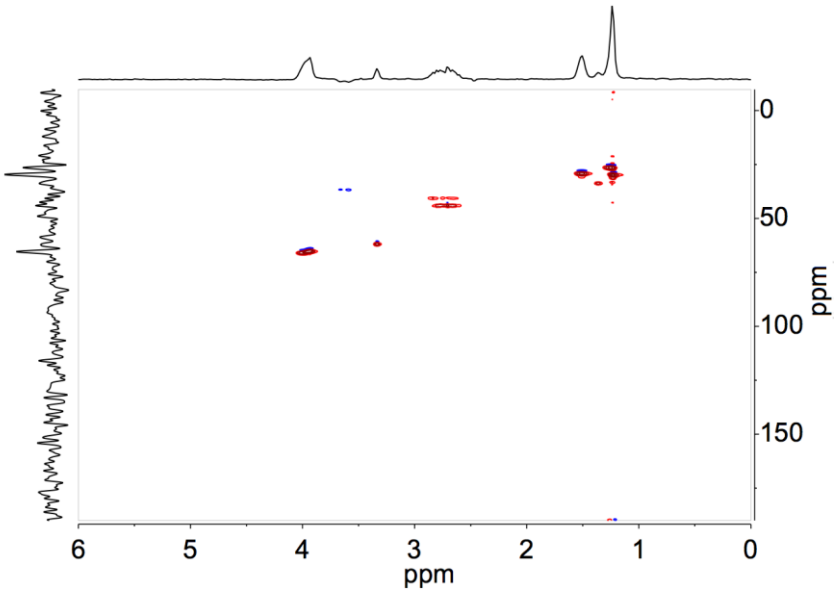


Figure S11. HSQC 2D NMR spectrum of PTCO.

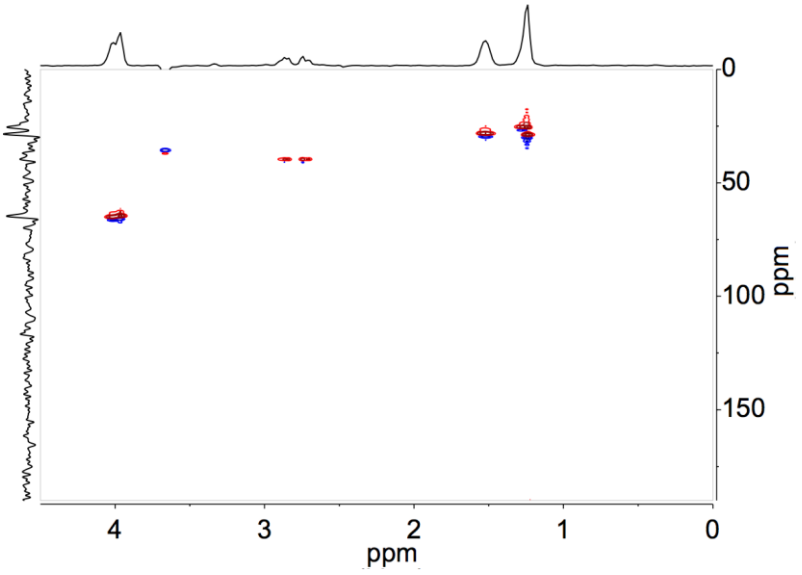


Figure S12. HSQC 2D NMR spectrum of PTO.

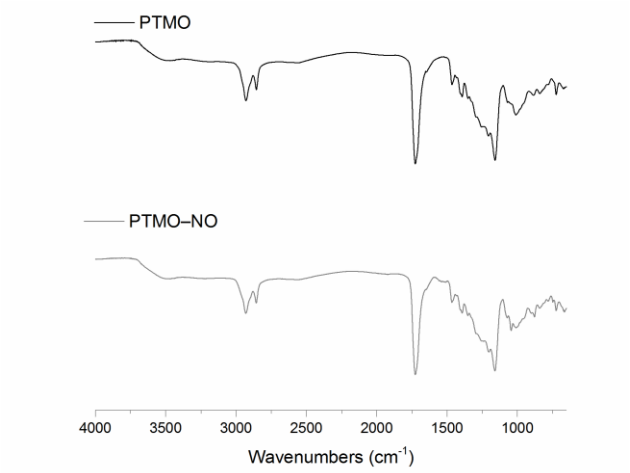


Figure S13. FTIR-ATR spectra of PTMO and PTMO–NO.

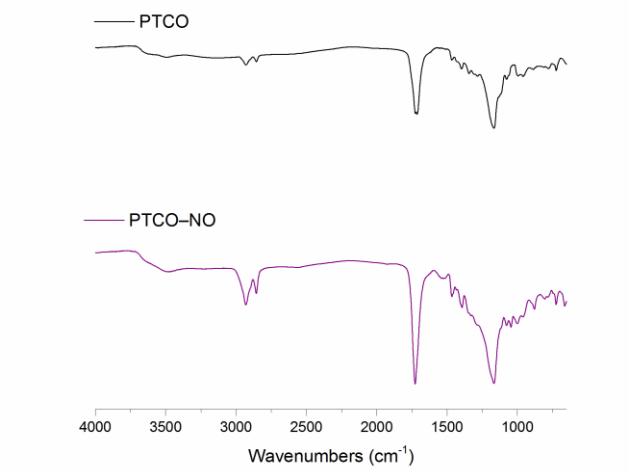


Figure S14. FTIR-ATR spectra of PTCO and PTCO–NO.

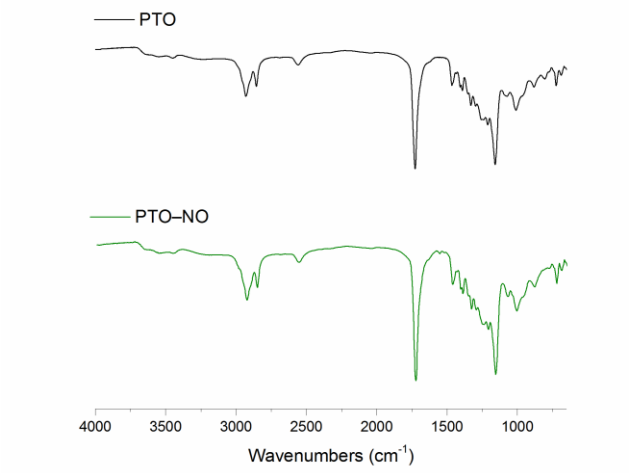


Figure S15. FTIR-ATR spectra of PTO and PTO–NO.

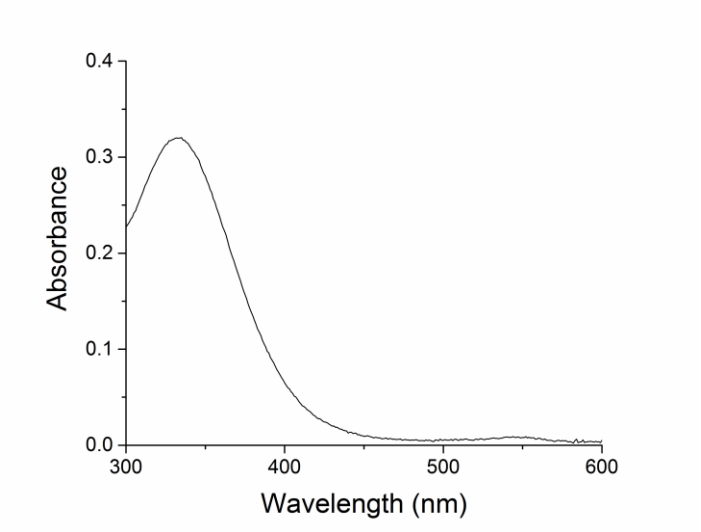


Figure S16. UV-Vis spectrum of PTMO–NO in DMSO. The spectrum depicts the characteristic transitions of *S*-nitrosothiols at 335 ($\pi \rightarrow \pi^*$) and 544 nm ($n_N \rightarrow \pi^*$).

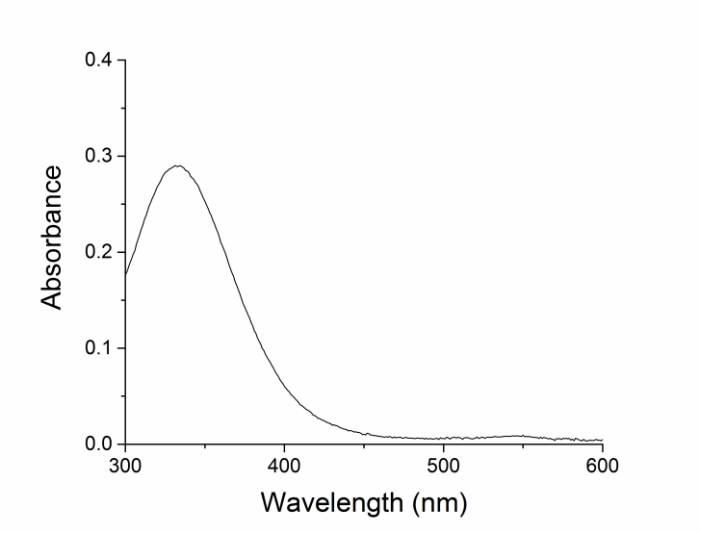


Figure S17. UV-Vis spectrum of PTCO–NO in DMSO. The spectrum depicts the characteristic transitions of *S*-nitrosothiols at 331 ($\pi \rightarrow \pi^*$) and 544 nm ($n_N \rightarrow \pi^*$).

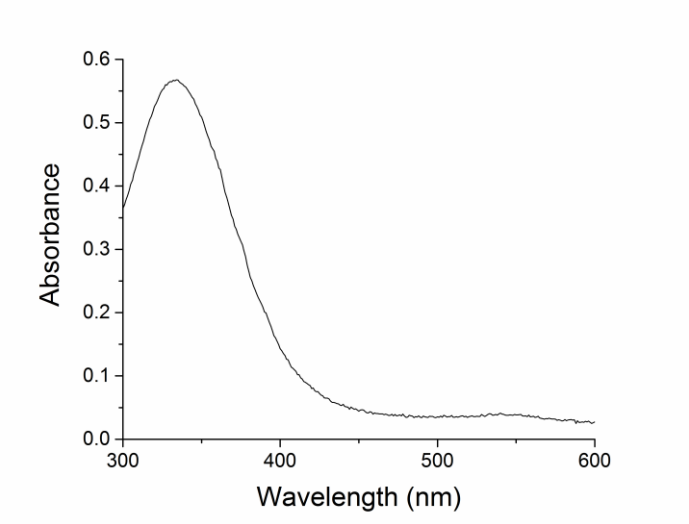
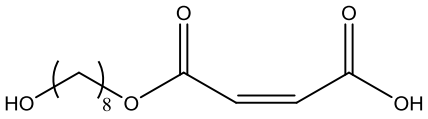
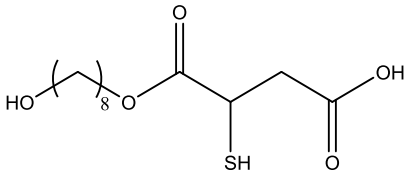


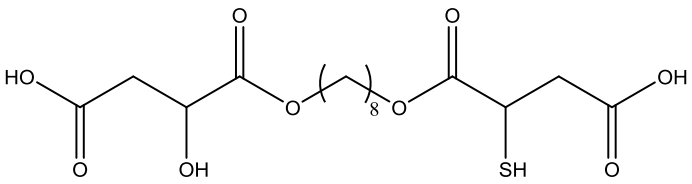
Figure S18. UV-Vis spectrum of PTO–NO in DMSO. The spectrum depicts the characteristic transitions of *S*-nitrosothiols at 333 ($\pi \rightarrow \pi^*$) and 540 nm ($n_N \rightarrow \pi^*$).



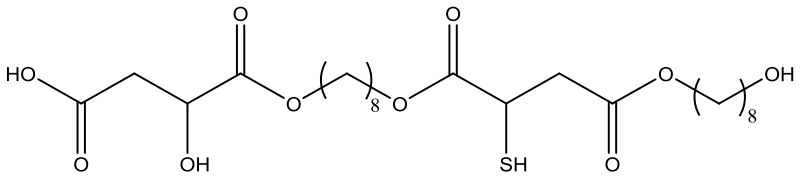
PTMO-P1, PTCO-P1, PTO-P1*‡
4-((8-hydroxyoctyl)oxy-4-oxobut-2-enoic acid



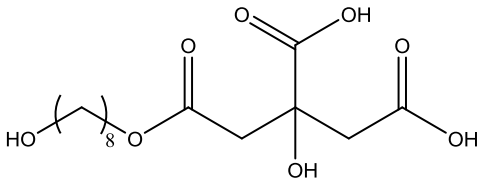
PTMO-P2, PTCO-P2, PTO-P2‡
4-((8-hydroxyoctyl)oxy)-3-mercapto-4-oxobutanoic acid



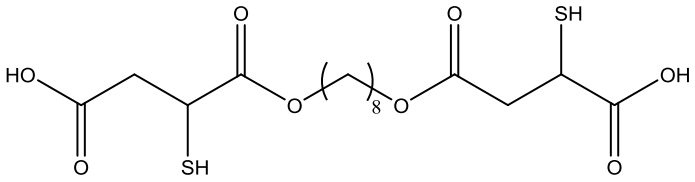
PTMO-P3, PTO-P3*
4-((8-((3-carboxy-3-hydroxypropanoyl)oxy)octyl)oxy)-2-mercapto-4-oxobutanoic acid



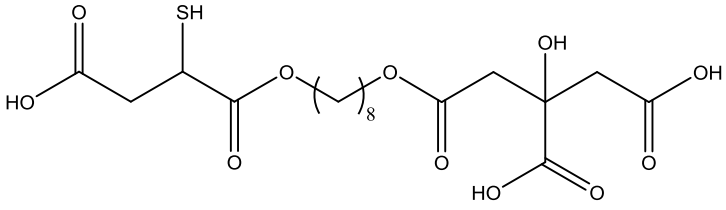
PTMO-P4, PTO-P4*
2-hydroxy-4-((8-((4-((8-hydroxyoctyl)oxy)-3-mercapto-4-oxobutanoyl)oxy)octyl)oxy)-4-oxobutanoic acid



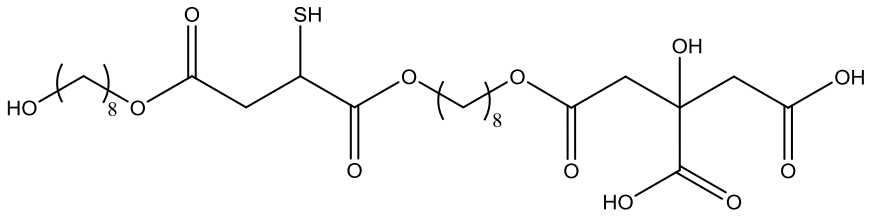
PTCO-P3
2-hydroxy-2-(2-((8-hydroxyoctyl)oxy)-2-oxoethyl)succinic acid



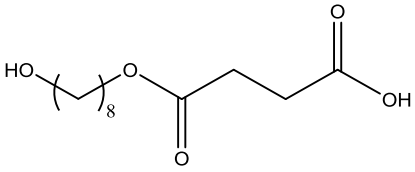
PTCO-P4
4-((8-((3-carboxy-2-mercaptopropanoyl)oxy)octyl)oxy)-2-mercapto-4-oxobutanoic acid



PTCO-P5
2-(2-((8-((3-carboxy-2-mercaptopropanoyl)oxy)octyl)oxy)-2-oxoethyl)-2-hydroxysuccinic acid



PTCO-P6
2-hydroxy-2-(2-((8-((4-((8-hydroxyoctyl)oxy)-2-mercapto-4-oxobutanoyl)oxy)octyl)oxy)-2-oxoethyl)succinic acid



PTCO-P7*†
4-((8-hydroxyoctyl)oxy)-4-oxobutanoic acid

Figure S19. Structures and names of degradation products identified using mass spectrometry. *Ions also found as byproducts from *S*-nitrosated polymers (PTMO–NO, PTCO–NO and PTO–NO). ‡Ions common to all polymers (PTMO, PTMO–NO, PTCO, PTCO–NO, PTO and PTO–NO) corresponding to dimers composed of the bonded monomers. †Ion only found as byproduct from the *S*-nitrosated polymer PTCO–NO.

Table S1. Viable bacteria (CFU/mL) obtained after 6 and 24 h exposure to *S*-nitrosated polymers. For all experiments, $n \geq 6$ and results are reported as the mean ± standard deviation.

	Viable Bacteria (CFU/mL)			
	E. coli		*S. aureus*	
	6 h	24 h	6 h	24 h
PC [a]	$(8.0 \pm 1.2) \times 10^8$	$(5.6 \pm 2.4) \times 10^8$	$(9.1 \pm 5.0) \times 10^7$	$(1.1 \pm 0.4) \times 10^9$
PTMO–NO (**1a**)	1	1	1	1
PTCO–NO (**2a**)	$(5.2 \pm 6.4) \times 10^6$	1	1	1
PTO–NO (**3a**)	$(3.0 \pm 1.4) \times 10^3$	$(3.4 \pm 3.7) \times 10^4$	1	1

[a] Positive control (PC) represents the viable bacteria in the absence of polymer. A value of 1 represents the limit of detection for this technique.