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/ppm (400 MHz, DMSO-$d_6$): 12.73 (−CO$_2$H), 6.67–6.73 (−HC=CH−), 3.94–4.07 (−OC$_2$H$_2$−), 3.72–3.89 (−S−CH−CO$_2$−), 3.32–3.35 (−CH$_2$OH), 2.58–2.91 (−CH$_2$CO$_2$−), 2.49 (DMSO), 1.52–1.60 (−CH$_2$−(CH$_2$)$_4$−CH$_2$−), 1.34–1.39 (−CH$_2$−CH$_2$OH), 1.24 (−(CH$_2$)$_4$−).

**Figure S2.** $^1$H NMR spectrum of PTCO. $^1$H NMR δ/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$_2$OH), 2.61–2.91 (−CH$_2$CO$_2$−), 2.49 (DMSO), 1.51–1.53 (−CH$_2$−(CH$_2$)$_4$−CH$_2$−), 1.36–1.39 (−CH$_2$−CH$_2$OH), 1.25 (−(CH$_2$)$_4$−).
Figure S3. $^1$H NMR spectrum of PTO. $^1$H NMR δ/ppm (400 MHz, DMSO-d$_6$): 3.94–4.06 (–OC$_2$H–), 3.66–3.70 (–S–CH–CO$_2$–), 2.71–2.91 (–CH$_2$CO$_2$–), 2.49 (DMSO), 1.57 (–CH–(CH$_2$)$_4$–CH$_2$–), 1.25–1.30 (–(CH$_2$)$_4$–).

Figure S4. $^{13}$C NMR spectrum of PTMO. $^{13}$C NMR δ/ppm (100 MHz, DMSO-d$_6$): 170.3–172.6 (–CO$_2$–), 130.4–133.6 (–H–C=CH–), 64.8–65.5 (–CH$_2$OH), 61.2 (–OCH$_2$–), 41.9–42.0 (–S–CH–CO$_2$–), 39.3–40.6 (DMSO), 35.9–37.1 (–CH$_2$CO$_2$–), 33.0 (–CH$_2$–CH$_2$OH), 29.0–29.3 (–(CH$_2$)$_2$–), 28.4–28.5 (–CH$_2$–(CH$_2$)$_4$–CH$_2$–), 25.7–25.9 (–(CH$_2$)$_2$–).
Figure S5. $^{13}$C NMR spectrum of PTCO. $^{13}$C NMR $\delta$/ppm (100 MHz, DMSO–d$_6$): 169.6–174.9 (–CO$_2$–), 72.9–73.3 (–C–OH), 64.4–65.3 (–OCH$_2$–), 61.2 (–CH$_2$OH), 41.9–42.0 (–CH$_2$CO$_2$–), 39.3–40.6 (DMSO), 35.8–35.9 (–S–CH–CO$_2$–), 33.0 (–(CH$_2$)$_2$–), 28.4–28.5 (–CH$_2$–(CH$_2$)$_4$–CH$_2$–), 25.6–25.9 (–(CH$_2$)$_2$–).

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Figure S8. COSY 2D NMR spectrum of PTCO.
Figure S9. COSY 2D NMR spectrum of PTO.

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Figure S17. UV-Vis spectrum of PTCO–NO in DMSO. The spectrum depicts the characteristic transitions of S-nitrosothiols at 331 (π → π*) and 544 nm (η_N → π*).
Figure S18. UV-Vis spectrum of PTO–NO in DMSO. The spectrum depicts the characteristic transitions of S-nitrosothiols at 333 (π → π*) and 540 nm (nN → π*).

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-oxobutanooyl)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-hydroxy succinic 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.

<table>
<thead>
<tr>
<th>Viable Bacteria (CFU/mL)</th>
<th>6 h</th>
<th>24 h</th>
<th>6 h</th>
<th>24 h</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>E. coli</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PC(^a)</td>
<td>(8.0 ± 1.2) ( \times ) ( 10^8 )</td>
<td>(5.6 ± 2.4) ( \times ) ( 10^8 )</td>
<td>(9.1 ± 5.0) ( \times ) ( 10^7 )</td>
<td>(1.1 ± 0.4) ( \times ) ( 10^9 )</td>
</tr>
<tr>
<td>PTMO–NO (1a)</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>PTCO–NO (2a)</td>
<td>(5.2 ± 6.4) ( \times ) ( 10^6 )</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>PTO–NO (3a)</td>
<td>(3.0 ± 1.4) ( \times ) ( 10^3 )</td>
<td>(3.4 ± 3.7) ( \times ) ( 10^4 )</td>
<td>1</td>
<td>1</td>
</tr>
</tbody>
</table>

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