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Electronic Supplementary Information

Biodegradable citrate-based polyesters with *S*-nitrosothiol functional groups for nitric oxide release

J. P. Yapor,[a] A. Lutzke,[a] A. Pegalajar-Jurado,[a] B. H. Neufeld,[a] V. B. Damodaran,[a†] M. M. Reynolds*[a,b]

[a]Department of Chemistry and [b]School of Biomedical Engineering, Colorado State University, Fort Collins, CO 80523, USA. [†]Current address: New Jersey Center for Biomaterials, Rutgers University, Piscataway, NJ 08854, USA.

*Corresponding author. E-mail: melissa.reynolds@colostate.edu

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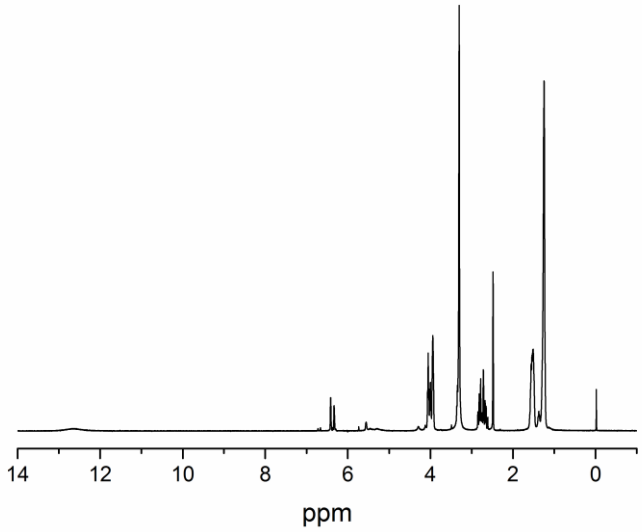

Figure S1. ^{1}H NMR spectrum of PCMO. ^{1}H NMR δ_H/ppm (400 MHz, DMSO-d_6): 1.20-1.65 (-(C**H$_2$**)$_6$-), 2.66-2.76 (-C**H$_2$**CO$_2$-), 3.95-4.03 (-O**CH$_2$**-), 6.35 (-**H**C=C**H**-), 12.6 (-CO$_2$**H**).

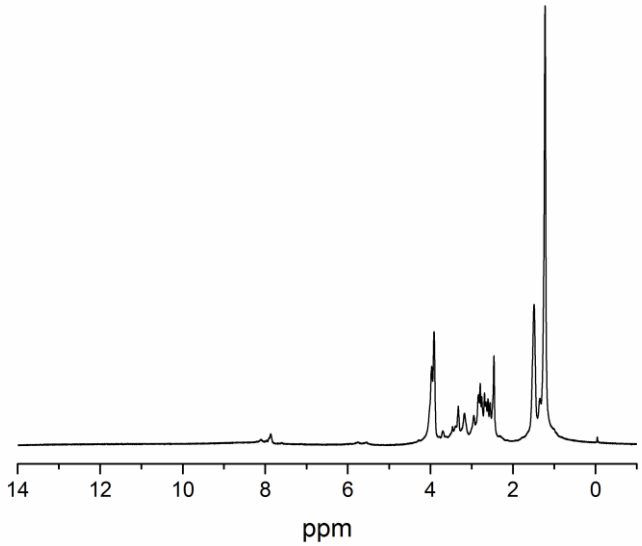

Figure S2. ^{1}H NMR spectrum of PCMO-cysteamine. ^{1}H NMR δ_H/ppm (400 MHz, DMSO-d_6): 1.20-1.65 (-(C**H$_2$**)$_6$-), 2.66-2.76 (-C**H$_2$**CO$_2$-), 2.98 (-C**H$_2$**SH), 3.22 (-(CO)NHC**H**-), 3.95-4.03 (-O-C**H$_2$**-), 6.35 (-**H**C=C**H**-), 7.82-7.92 (-(CO)N**H**-).

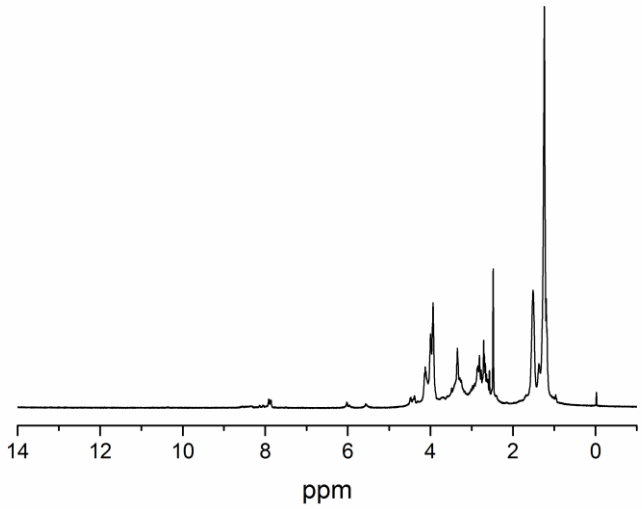

Figure S3. ^{1}H NMR spectrum of PCMO-ethyl cysteinate. ^{1}H NMR δ_H/ppm (400 MHz, DMSO-d_6): 1.18-1.22 (-C**H**$_3$) 1.20-1.65 (-(C**H**$_2$)$_6$-), 2.66-2.76 (-C**H**$_2$CO$_2$-), 3.70 (-C**H**$_2$SH), 4.42 (-(CO)NHC**H**-), 3.95-4.03 (-OC**H**$_2$-), 6.35 (-**H**C=C**H**-), 7.84-7.94 (-(CO)N**H**-).

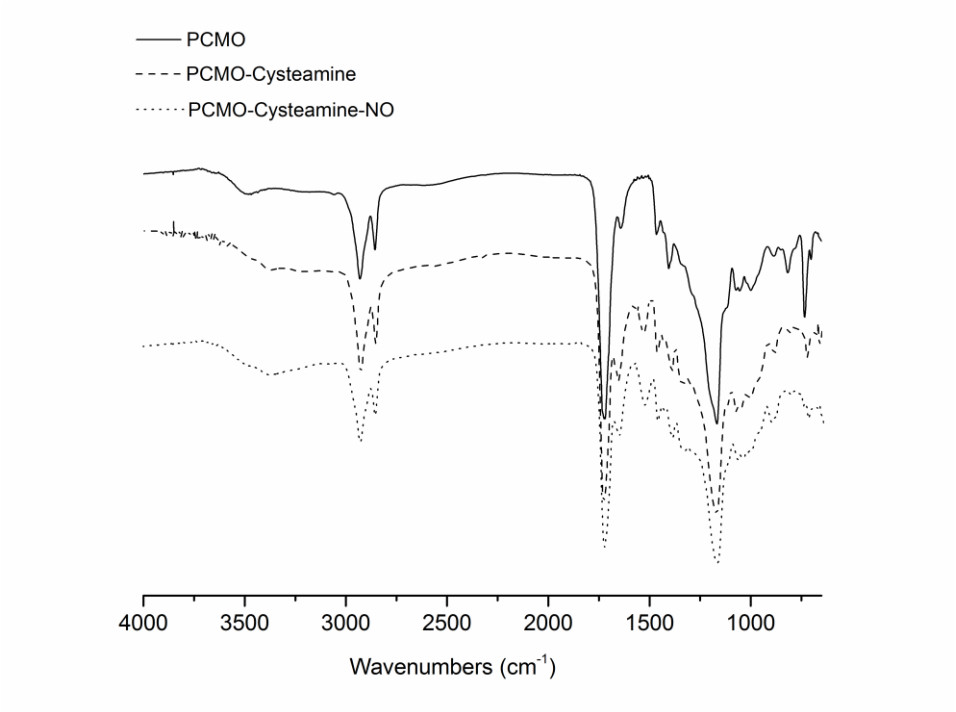

Figure S4. FTIR-ATR spectra of PCMO, PCMO-cysteamine, and PCMO-cysteamine-NO.

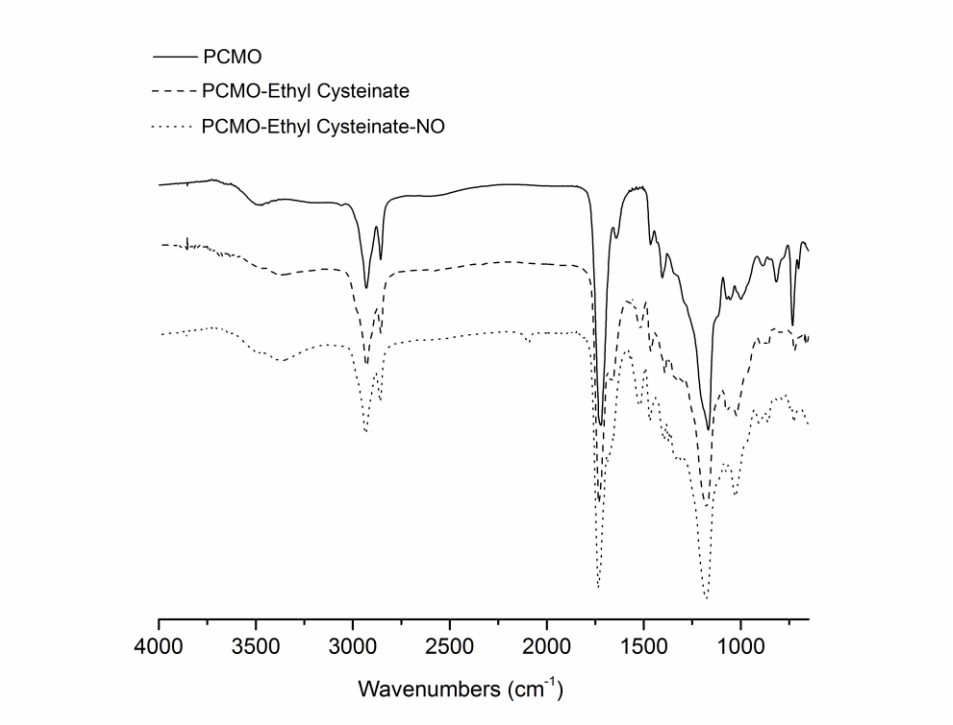

Figure S5. FTIR-ATR spectrum of PCMO, PCMO-ethyl cysteinate, and PCMO-ethyl cysteinate-NO.

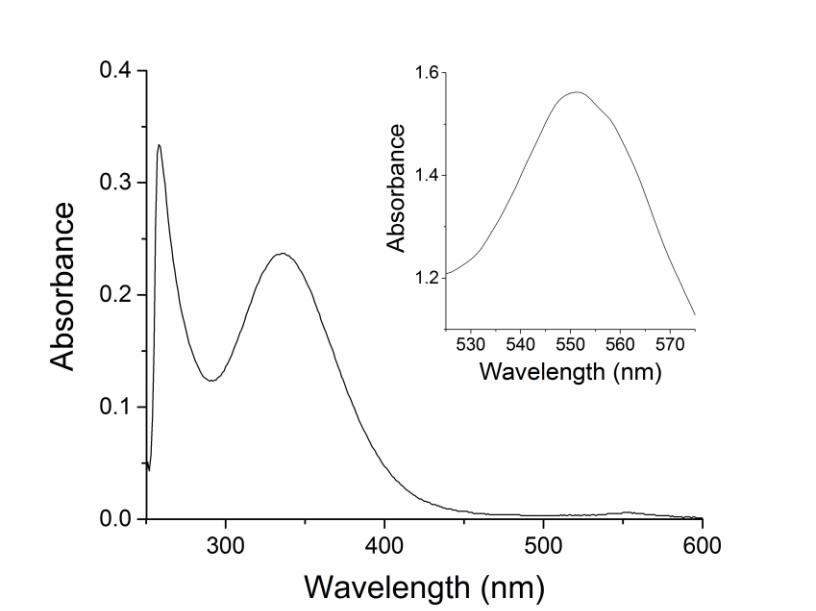

Figure S6. UV-Vis spectrum of PCMO-cysteamine-NO in DMSO. **Inset**: Diffuse reflectance UV-Vis spectrum. The spectra depict the characteristic transitions of *S*-nitrosothiols at 335 ($n_O \rightarrow \pi^*$) and 550 nm ($n_N \rightarrow \pi^*$). Diffuse reflectance was used to identify the peak corresponding to the $n_N \rightarrow \pi^*$ transition since the small molar extinction coefficient prevents unambiguous solution-phase measurements within the solubility range of the polymer.

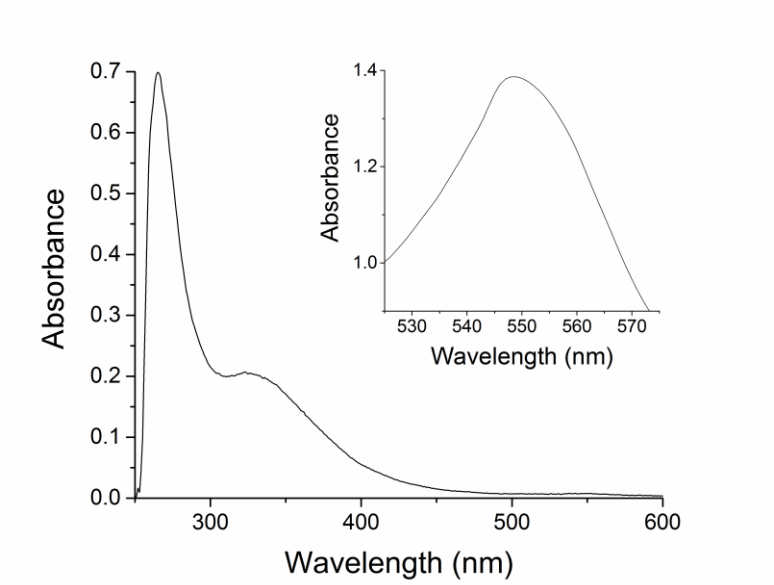

Figure S7. UV-Vis spectrum of PCMO-ethyl cysteinate-NO in DMSO. **Inset:** Diffuse reflectance UV-Vis spectrum. The spectra depict the characteristic transitions of *S*-nitrosothiols at 336 ($n_O \rightarrow \pi^*$) and 549 nm ($n_N \rightarrow \pi^*$). Diffuse reflectance was used to identify the peak corresponding to the $n_N \rightarrow \pi^*$ transition since the small molar extinction coefficient prevents unambiguous solution-phase measurements within the solubility range of the polymer.

Table S1. Hydrolytic degradation of PCMO and *S*-nitrosated derivatives.

		% Weight Remaining			
Material	Initial	Week 1	Week 2	Week 3	Week 4
PCMO	100	88.5 ± 0.7	77.4 ± 0.1	12.1 ± 3.0	1.70 ± 0.5
PCMO-CysAm-NO (2a)	100	77.7 ± 1.1	69.5 ± 1.1	56.7 ± 1.4	47.2 ± 3.8
PCMO-EtCys-NO (3a)	100	59.6 ± 1.1	57.2 ± 1.7	52.4 ± 2.0	48.6 ± 1.4

Hydrolytic degradation of the *S*-nitrosated materials was evaluated under physiological conditions (pH 7.4, 37 °C) in 10 mM PBS over 4 weeks. Each week, the buffer was replaced and the materials were lyophilized for 24 h before data collection. For all experiments, n ≥ 3 and results are reported as the mean ± SD.