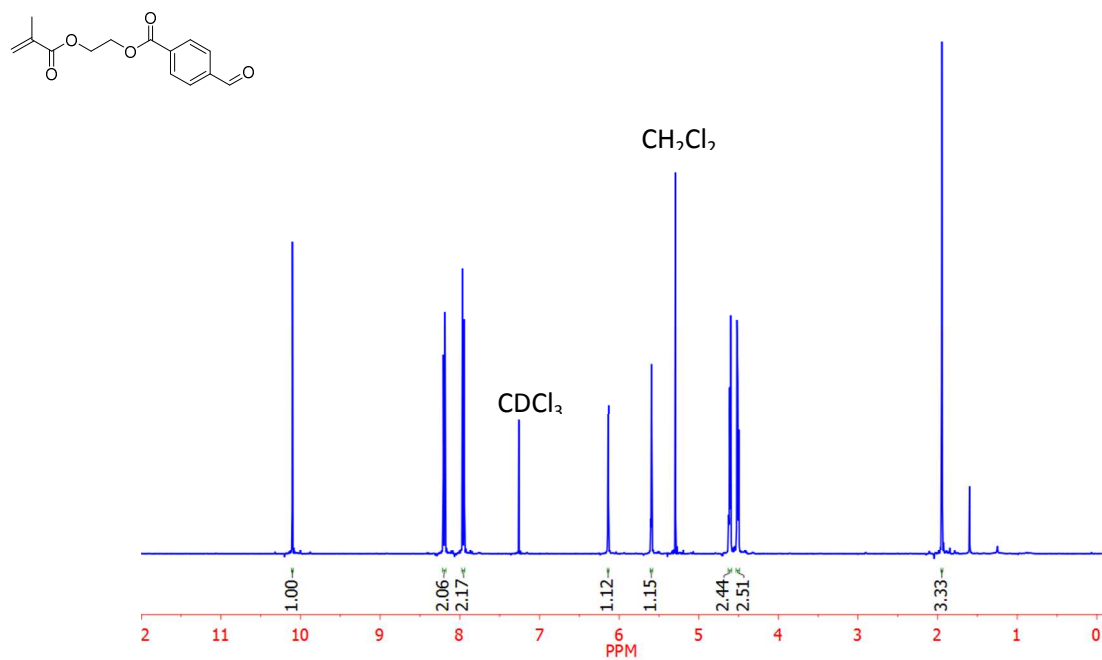


Supporting Information

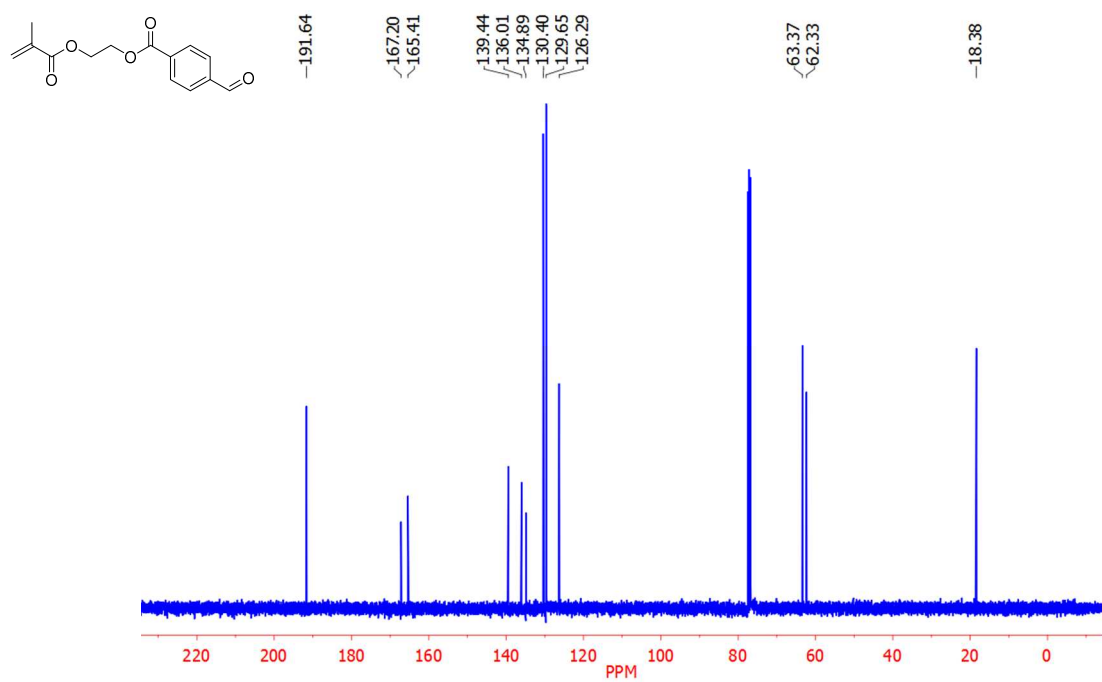
**Functionalization of Methacrylate Polymers with Thiooximes: A Robust Post-Polymerization Modification Reaction and a Method for the Preparation of H<sub>2</sub>S-Releasing Polymers**

Jeffrey C. Foster, John B. Matson

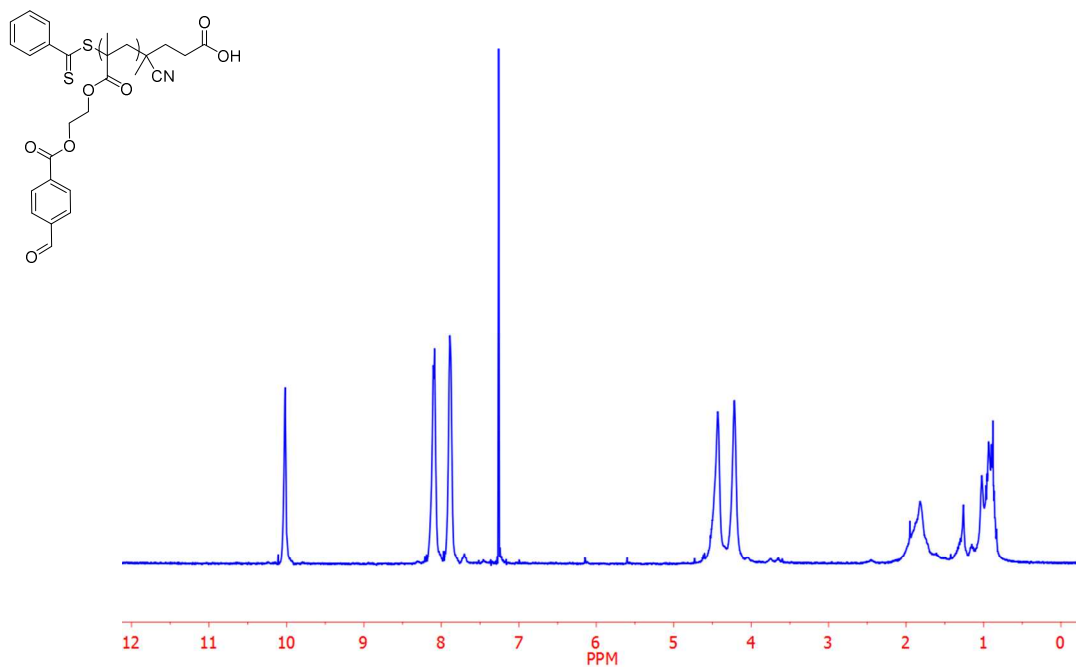
*Department of Chemistry, Virginia Tech, Blacksburg, VA 24061.*



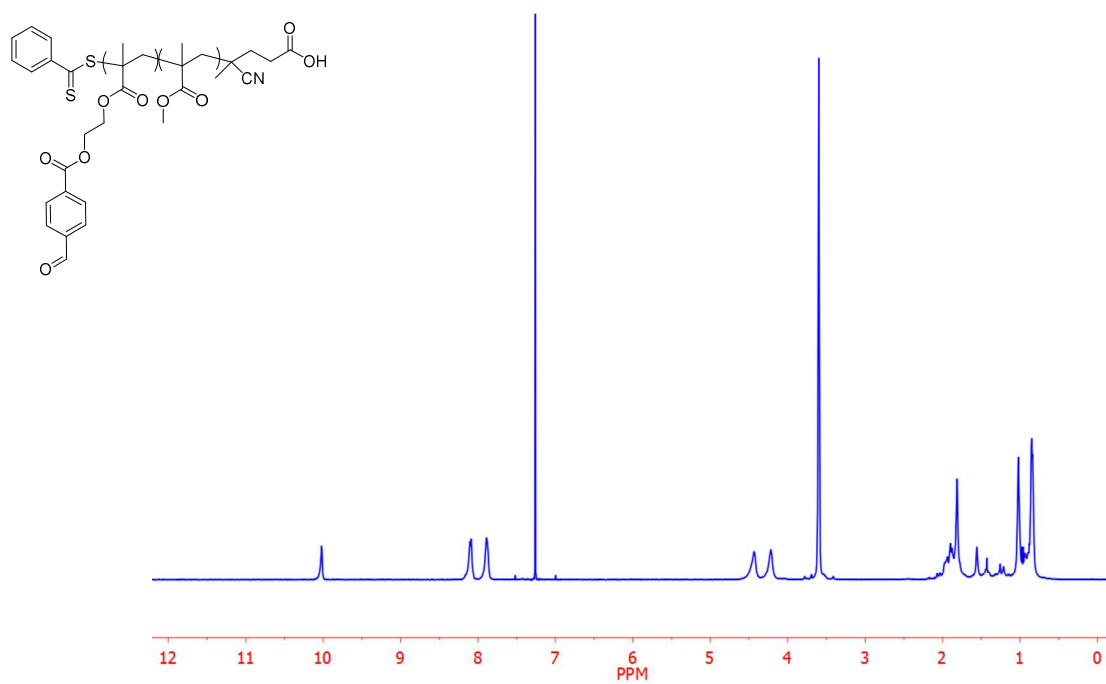
**Figure S1.**  $^1\text{H}$  NMR of FBEMA in  $\text{CDCl}_3$ .



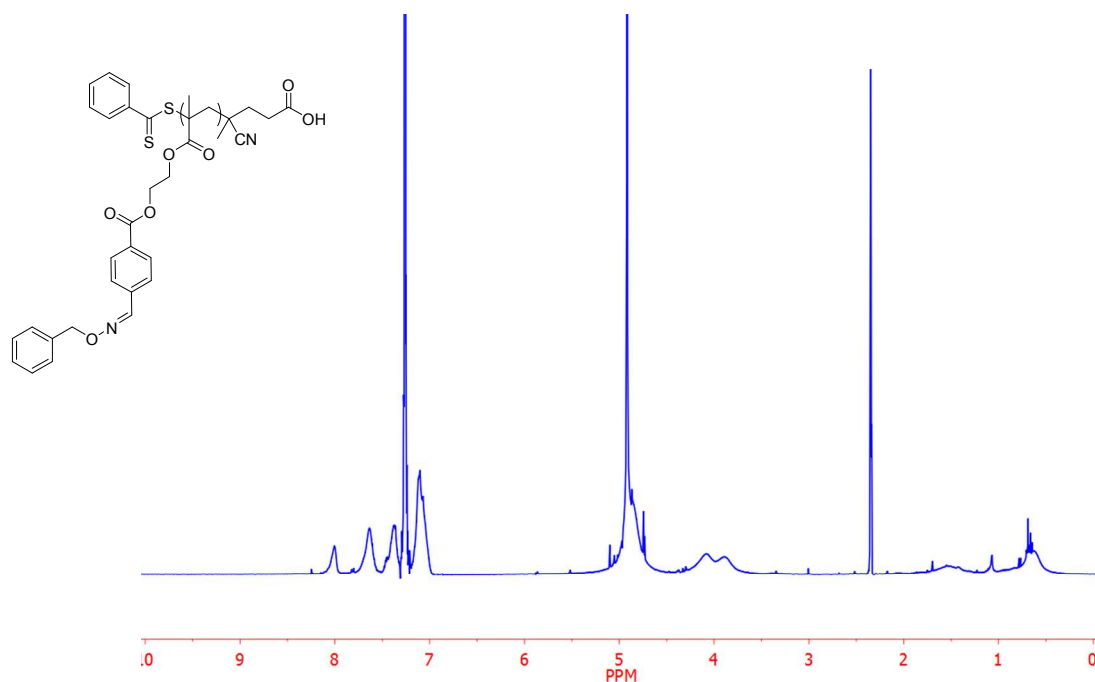
**Figure S2.**  $^{13}\text{C}$  NMR of FBEMA in  $\text{CDCl}_3$ .



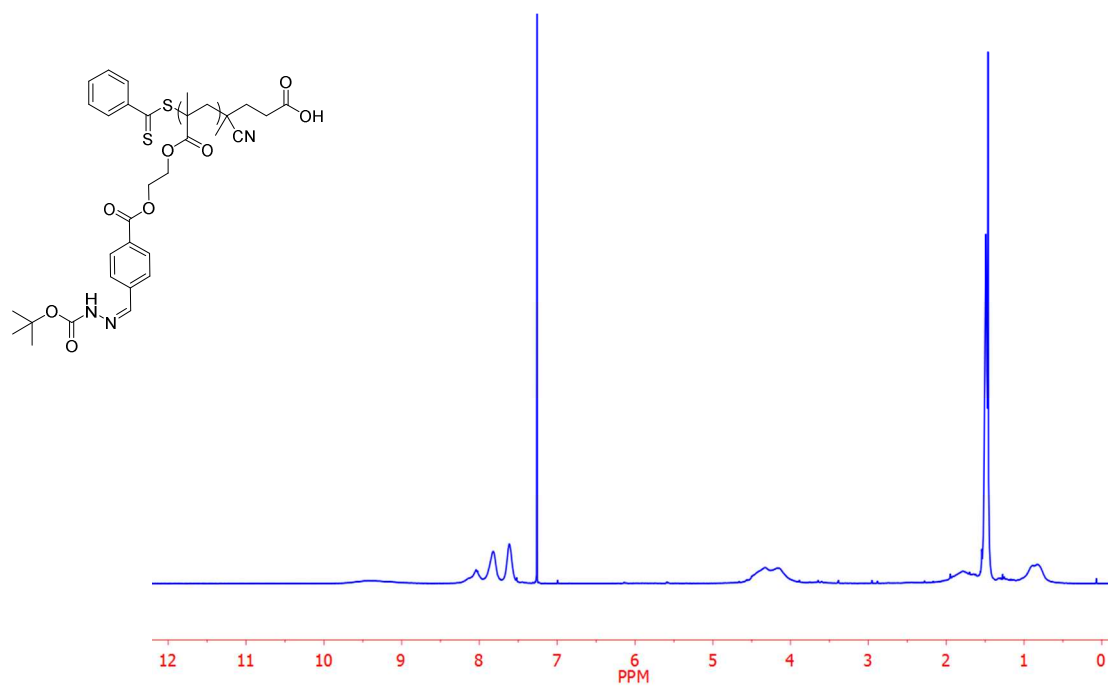
**Figure S3.**  $^1\text{H}$  NMR of poly(FBEMA) in  $\text{CDCl}_3$  (P2).



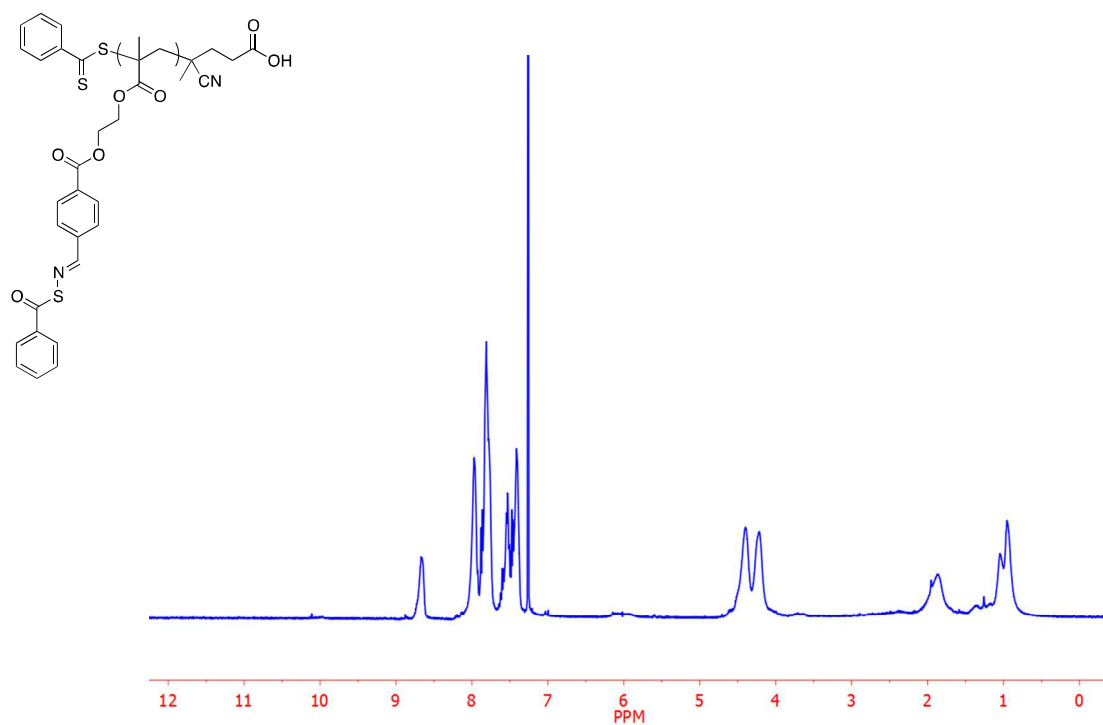
**Figure S4.**  $^1\text{H}$  NMR of poly(FBEMA-b-MMA) in  $\text{CDCl}_3$  (P4).



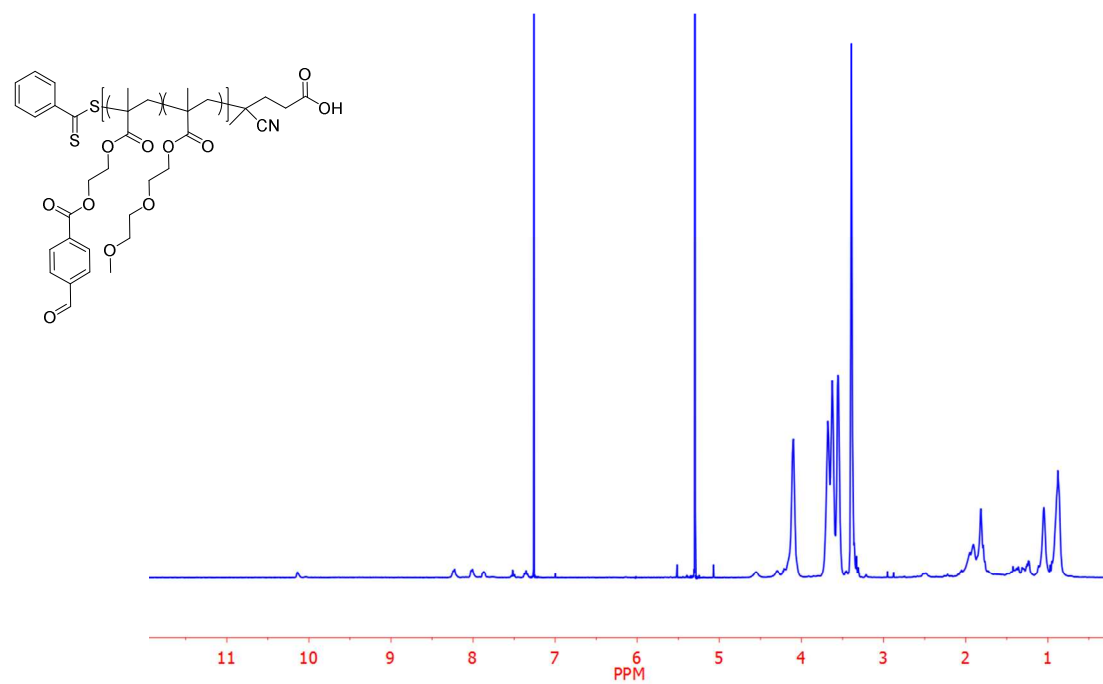
**Figure S5.**  $^1\text{H}$  NMR of *O*-hydroxylamine-modified poly(FBEMA) in  $\text{CDCl}_3$  (**P2o**).



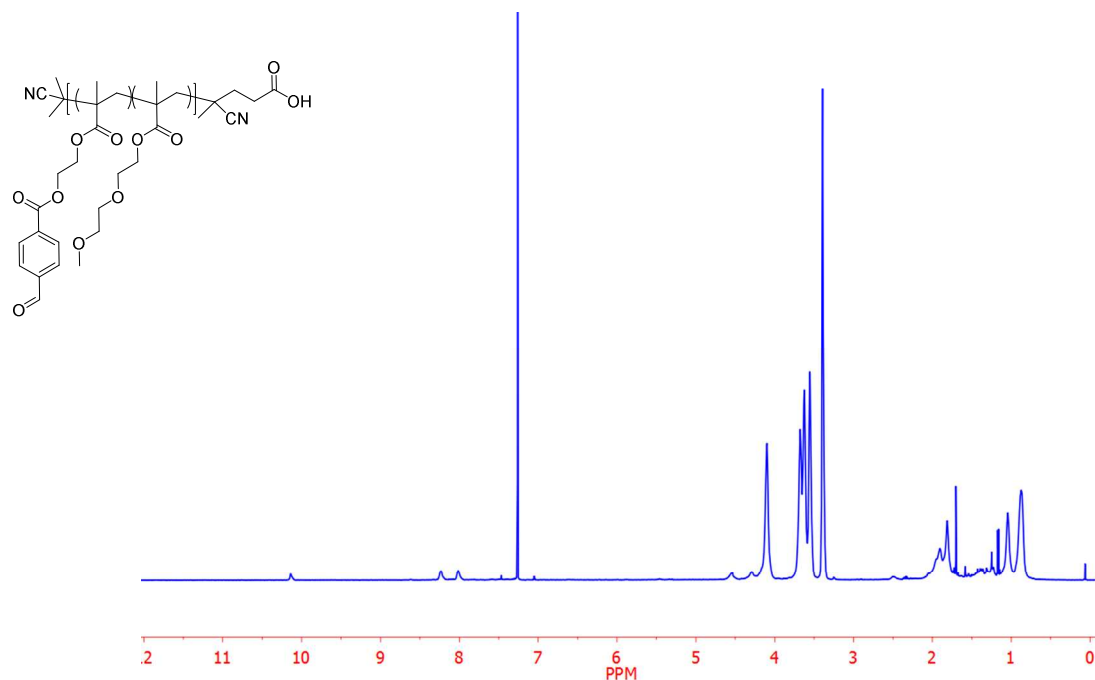
**Figure S6.**  $^1\text{H}$  NMR of hydrazone-modified poly(FBEMA) in  $\text{CDCl}_3$  (**P2h**).



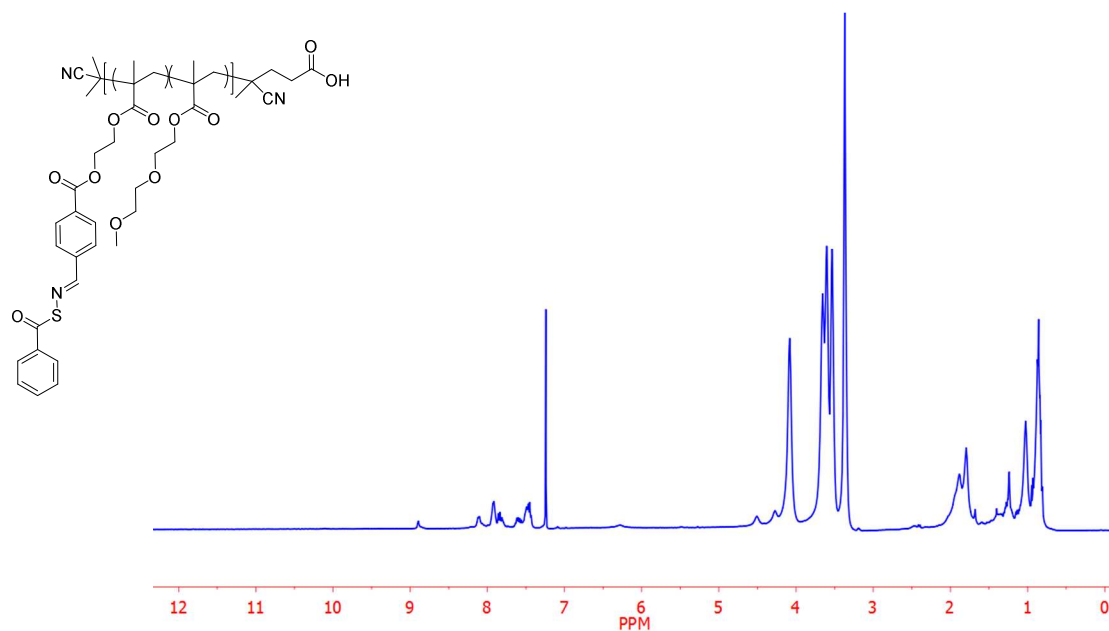
**Figure S7.**  $^1\text{H}$  NMR of thiooxime-modified poly(FBEMA) in  $\text{CDCl}_3$  (P2t).



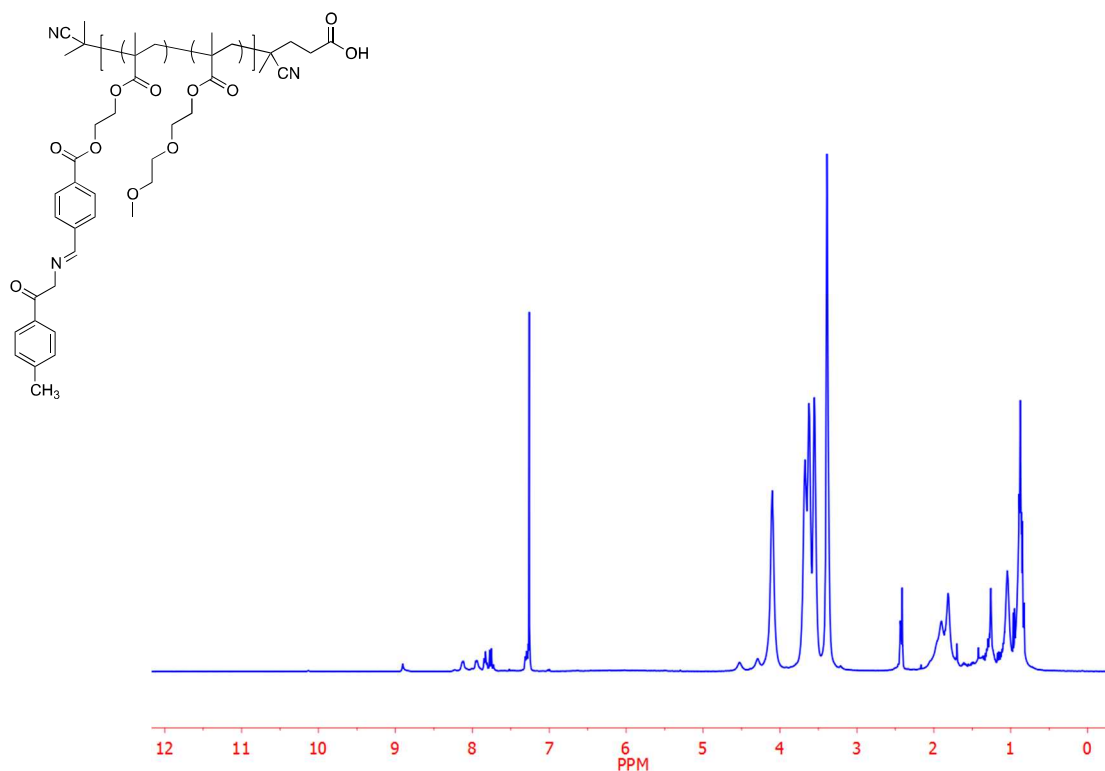
**Figure S8.**  $^1\text{H}$  NMR of poly(FBEMA-co-MEO<sub>2</sub>MA) in  $\text{CDCl}_3$  (P5).



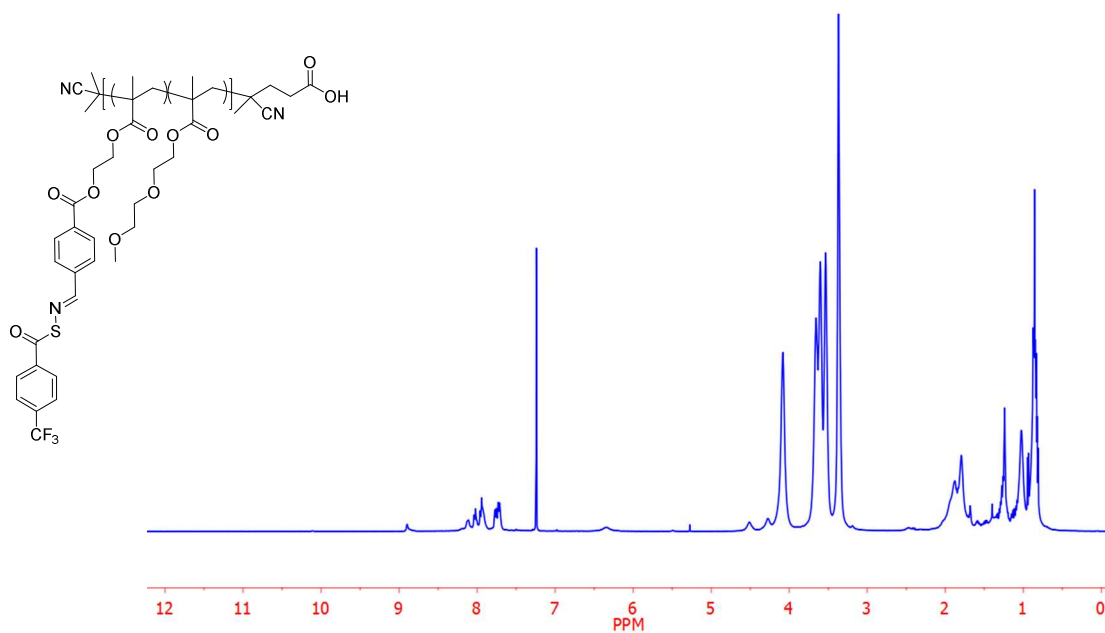
**Figure S9.** <sup>1</sup>H NMR of poly(FBEMA-*co*-MEO<sub>2</sub>MA) following end group removal with AIBN in CDCl<sub>3</sub>.



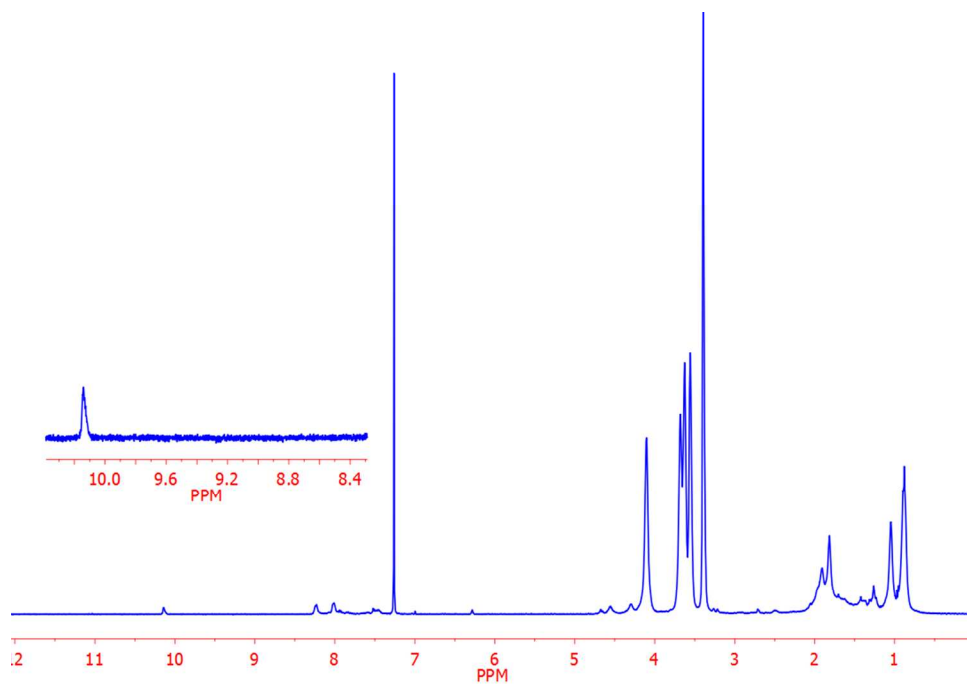
**Figure S10.** <sup>1</sup>H NMR of poly(FBEMA-*co*-MEO<sub>2</sub>MA) following end group removal with AIBN and conjugation to SATHA in CDCl<sub>3</sub> (**P6**).



**Figure S11.** <sup>1</sup>H NMR of poly(FBEMA-*co*-MEO<sub>2</sub>MA) following end group removal with AIBN and conjugation to SATHA in CDCl<sub>3</sub> (**P7**).

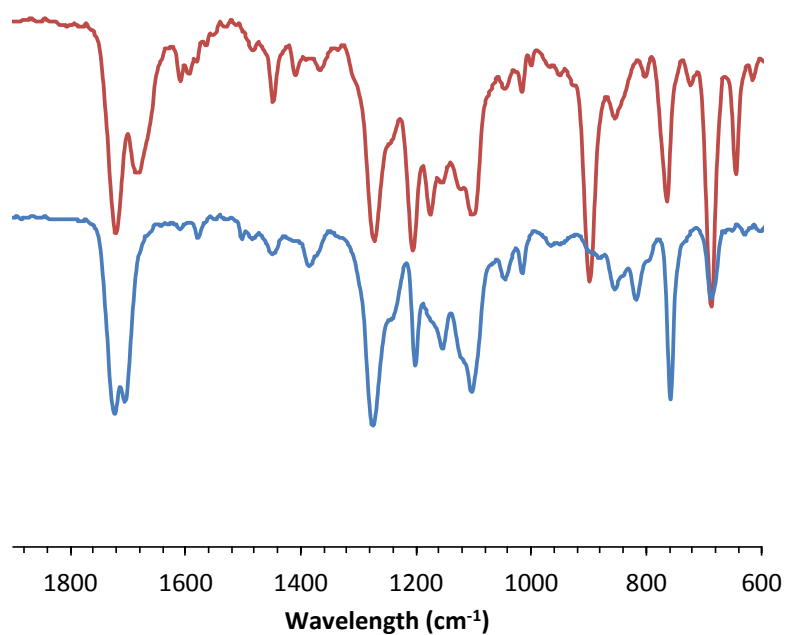


**Figure S12.** <sup>1</sup>H NMR of poly(FBEMA-*co*-MEO<sub>2</sub>MA) following end group removal with AIBN and conjugation to SATHA in CDCl<sub>3</sub> (**P8**).

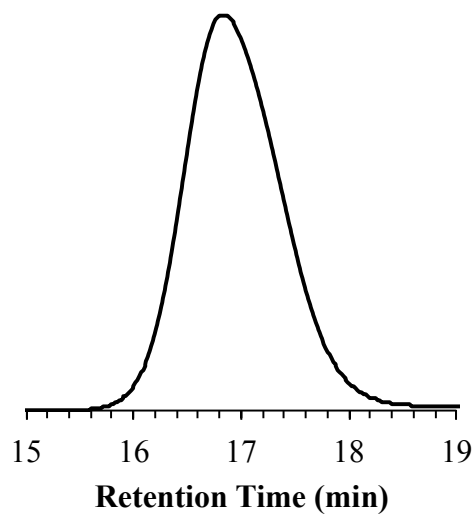


**Figure S13.** <sup>1</sup>H NMR of **P6** following reaction with glutathione. Quantitative conversion of thiooxime to aldehyde is observed based on the disappearance of the thiooxime peak at 8.67 ppm and appearance of the aldehyde peak at 10.02 ppm.

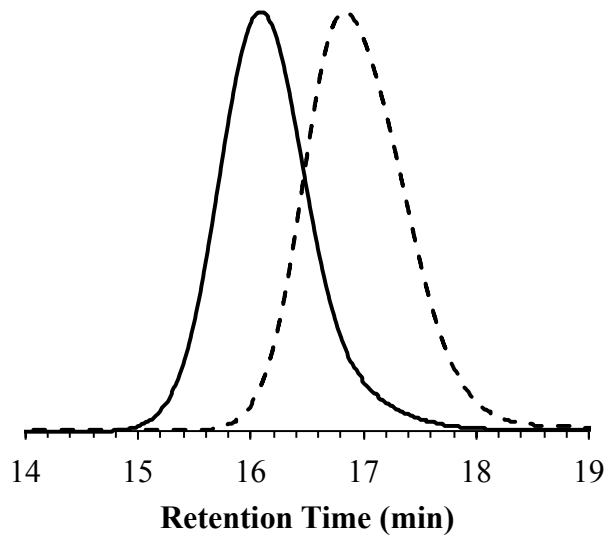




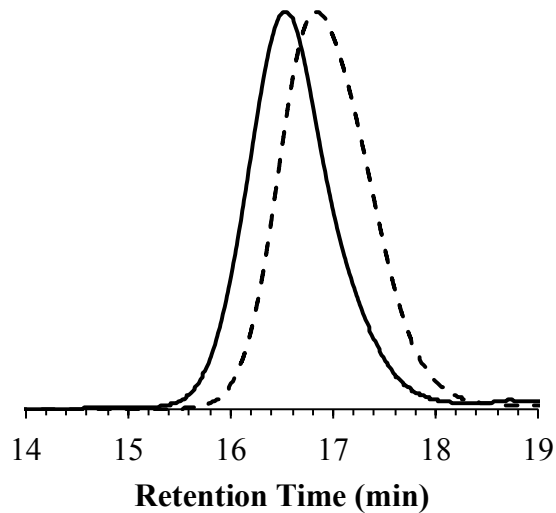
**Figure S14.** IR spectra of **P2** (blue trace) and the same polymer following post polymerization reaction with SATHA (**P2t**) (red trace). The appearance of a peak at 1608 cm<sup>-1</sup> corresponds to the stretching frequency of the thiooxime C=N bond.



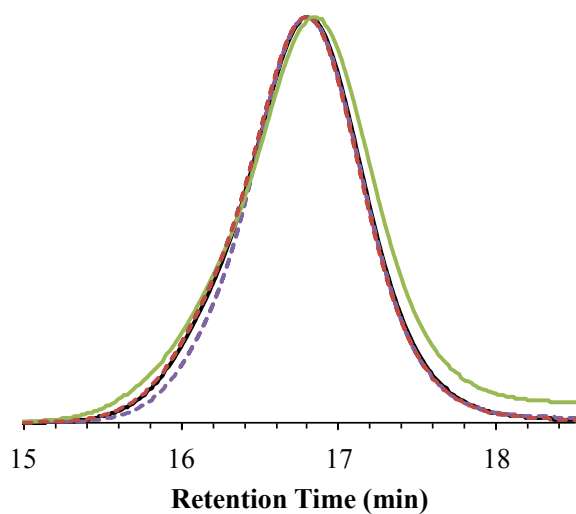
**Figure S15.** GPC trace of **P2** in THF ( $M_n = 17,300$  g/mol,  $\bar{D} = 1.12$ ,  $dn/dc = 0.140$ , [FBEMA]:[CTA]:[AIBN] = 300:1:0.2).



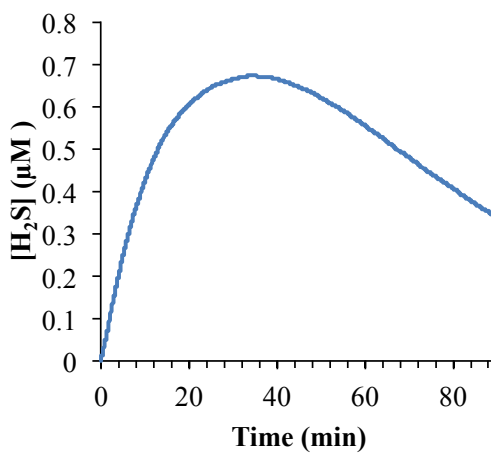
**Figure S16.** GPC trace of **P2** (dashed line) chain extended with MMA (**P4**) (solid line) in THF ( $M_n = 27,200$  g/mol,  $\bar{D} = 1.11$ ,  $dn/dc = 0.119$ ,  $[FBEMA]:[CTA]:[AIBN] = 2000:1:0.2$ ).



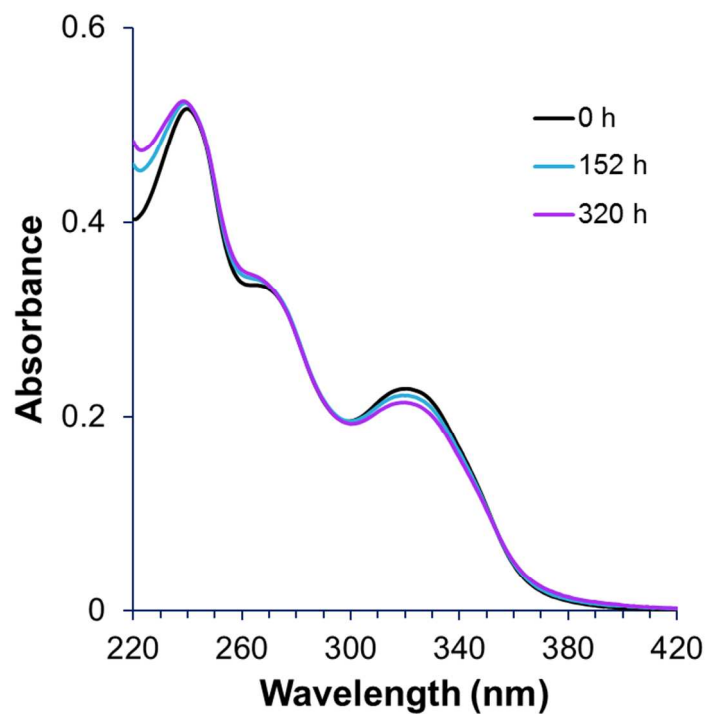
**Figure S17.** GPC trace of **P2t** (dashed line) following conjugation with SATHA (solid line) in THF ( $M_n = 25,900$  g/mol,  $\bar{D} = 1.12$ ,  $dn/dc = 0.188$ ).



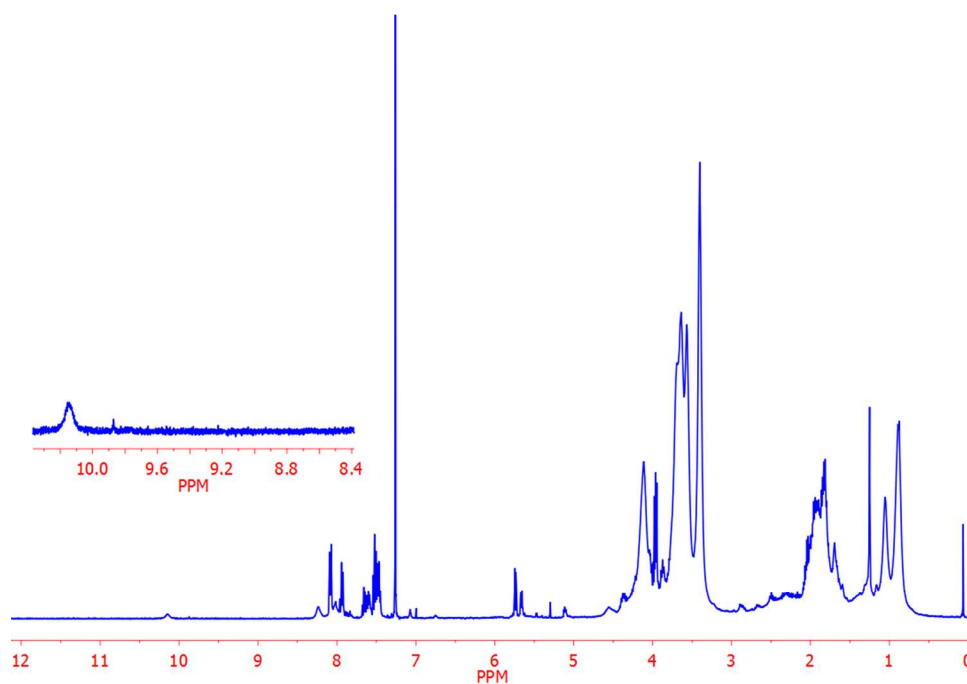
**Figure S18.** GPC traces of **P5** following chain end removal with AIBN (red dashed trace,  $M_n = 11,900$ ,  $\bar{D} = 1.19$ ,  $dn/dc = 0.079$ ). The resulting polymer was reacted with three different SATHAs with various substituents at the para position of the SATHA ring (*p*-H, **P6**, green trace:  $M_n = 13,800$  g/mol,  $\bar{D} = 1.14$ ,  $dn/dc = 0.085$ ; *p*-CH<sub>3</sub>, **P7**, purple dashed trace:  $M_n = 12,600$  g/mol,  $\bar{D} = 1.11$ ,  $dn/dc = 0.081$ ; *p*-CF<sub>3</sub>, **P8**, black trace:  $M_n = 11,800$  g/mol,  $\bar{D} = 1.15$ ,  $dn/dc = 0.078$ ).



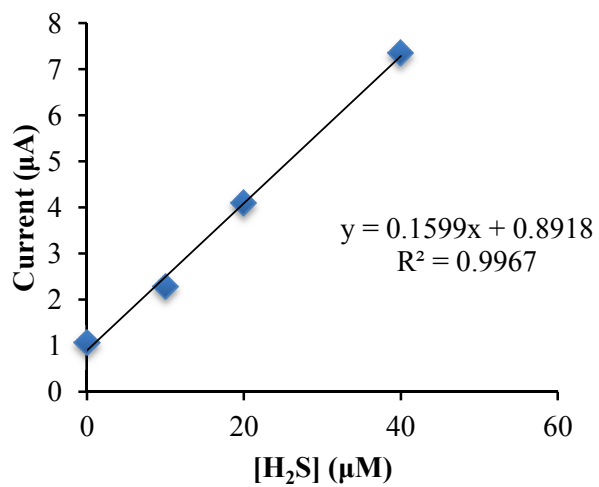
**Figure S19.** H<sub>2</sub>S release profile of **P6** (10  $\mu$ M) in the presence of 1 mM glutathione in PBS buffer (pH = 7.4).



**Figure S20.** Hydrolysis of **P2t** in 30% ACN in 2 mM phosphate buffer (pH 7.4) at 25  $\mu$ M starting *S*-aroylthiooxime concentration. Only select time points are shown for clarity. The peak absorbance at 320 nm is assigned to the *S*-aroylthiooxime based on previous work.<sup>1</sup> At 320 h only 4% of the *S*-aroylthiooxime has been hydrolyzed.



**Figure S21.**  $^1\text{H}$  NMR spectrum of **P6** following hydrolysis of the thiooxime bond for 48 h in THF + 10% HCl solution (2.5 M). Quantitative conversion of thiooxime to aldehyde is observed based on the disappearance of the thiooxime peak at 8.67 ppm and appearance of the aldehyde peak at 10.02 ppm.



**Figure S22.** Calibration of  $\text{H}_2\text{S}$ -selective microelectrode.

## References:

- (1) Foster, J. C.; Powell, C. R.; Radzinski, S. C.; Matson, J. B. *Org. Lett.* **2014**, *16*, 1558.