Supporting Information

Synthesis of biobased and versatile monomers from itaconic acid and homocysteine thiolactone and their applications in step-growth and radical polymerization approaches.

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Table S1. Reaction conditions for the synthesis of monomer M3.

Entry	Coupling agent	[IA]:[HTL]:[CA]	Solvent	pH	T° (°C)	Time	Product M3	Yield (%)
1	None	1:2:0	H_2O	8	25	24	No	-
2	PyBOP	1:2:2.1	DMSO	-	25	144	No	-
3	EDC	1:2.5:1.2	H_2O	8	25	24	No	-
4	EDC	1:2.5:1.2	H_2O	8	60	24	No	-
5	EDC	1:2.5:2.5	H_2O	4.5	25	24	No	-
6	EDC + DMAP	1:2.1:2.1	H_2O	6	25	24	No	-
7	EDC + DMAP	1:2.1:2.1	H_2O	8	25	24	No	-
8	EDC + HOBT	1:2.1:2.1	H_2O	4.5	25	21	No	-
9	EDC + HOBT	1:2.1:2.1	H_2O	7	25	4.5	Yes + side product	-
10	EDC + HOBT	1:2.1:2.1	H_2O	6	25	3.5	Yes	5
11	EDC + HOBT	1:2.1:2.1	H_2O	6	25	23	Yes	3
12	DMTMM	1:2.1:2.1	H_2O	8	25	4	Yes + side product	-
13	DMTMM	1:2.1:2.1	H_2O	6	25	4	Yes	12-20

Table S2. Maximum amount of M1 that can be dissolved in 1.0 mL of a selected solvent (visual determination).

Solvent	Mass (mg)
Deionized Water	5
Methanol	10
DMSO	500
DMF	100
DMAC	200
Ethanol	10
Acetone	-
Ethyl acetate	-
THF	10
$CHCl_3$	-
Toluene	-
Anisole	-

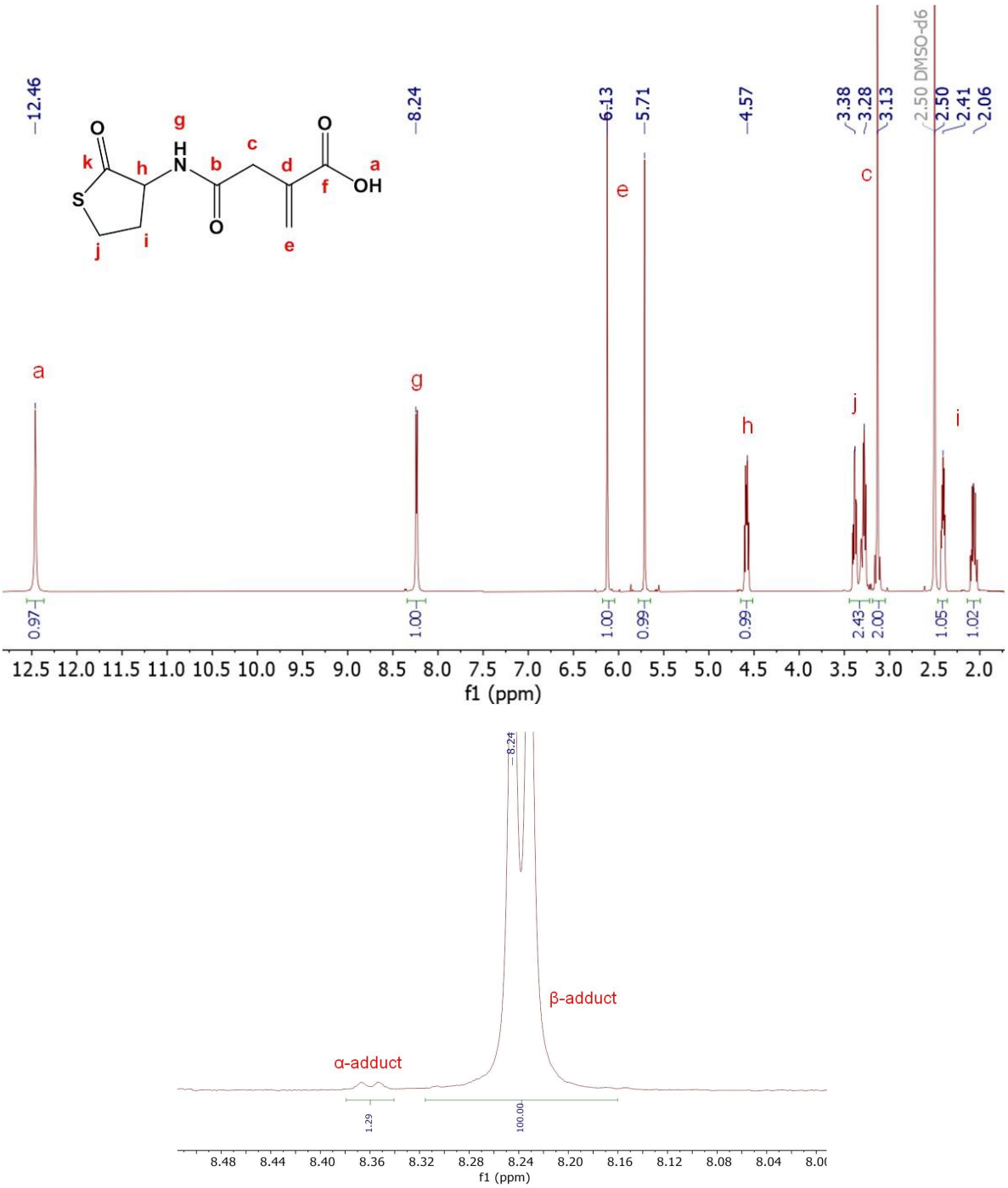


Figure S1. ^{1}H NMR spectrum of monofunctional monomer M1 in DMSO-d_6 at 25°C.

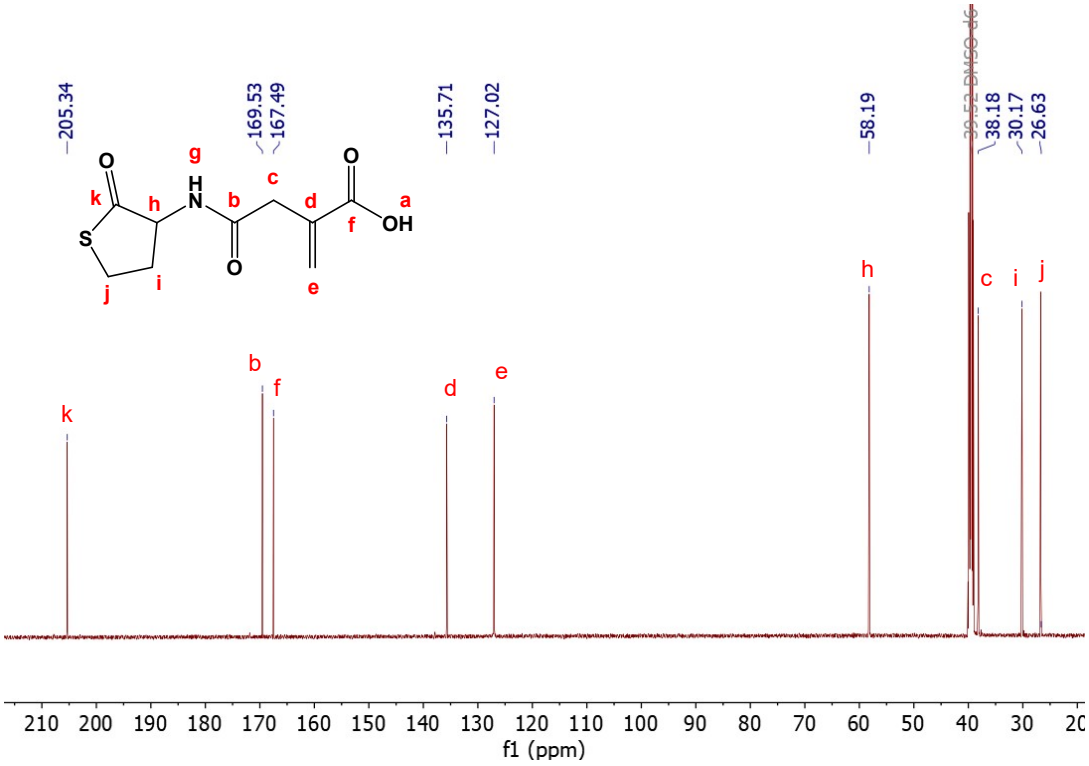


Figure S2. ^{13}C NMR spectrum of monofunctional monomer M1 in DMSO-d_6 at 25°C.

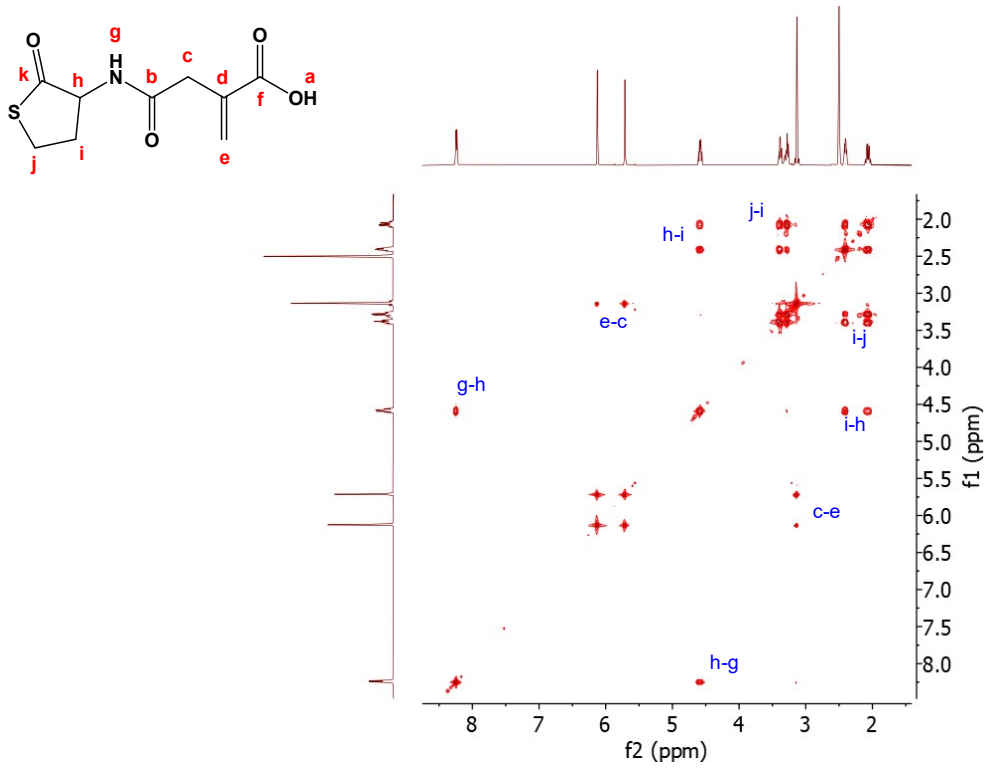


Figure S3. COSY NMR spectrum of monofunctional monomer M1 in DMSO-d_6 at 25°C.

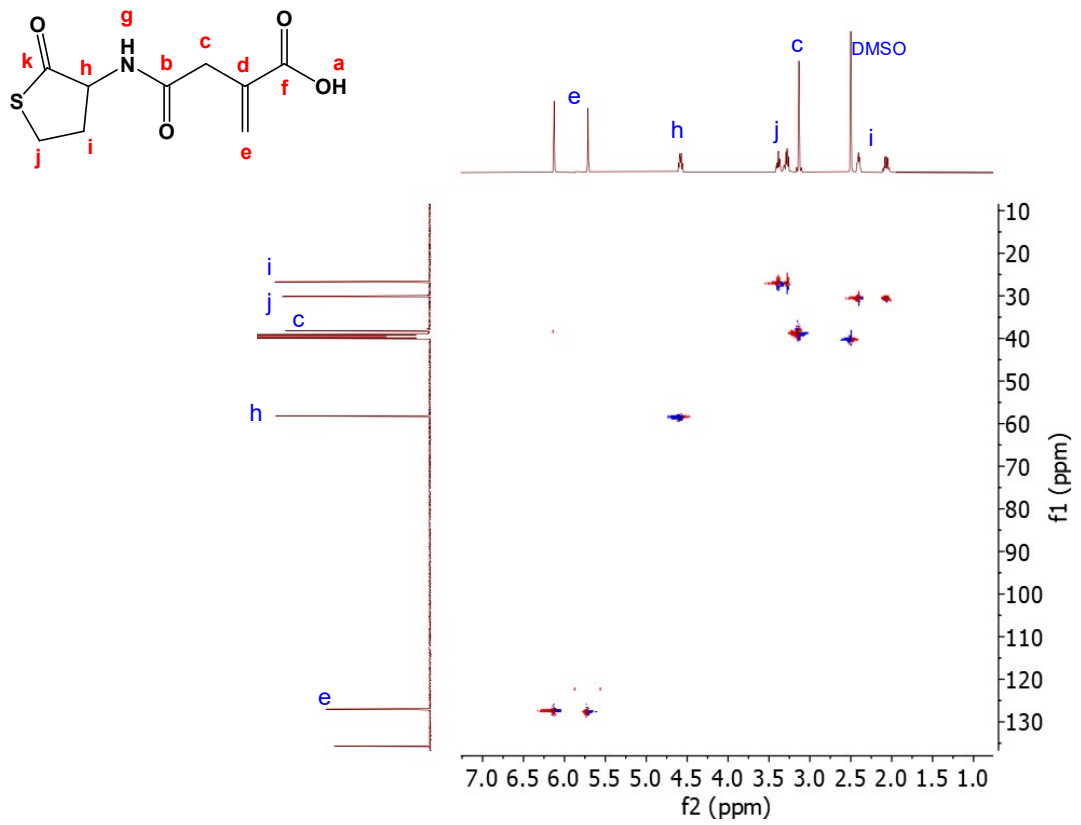


Figure S4. ^{1}H-^{13}C HSQC NMR spectrum of monofunctional monomer M1 in DMSO-d_6 at 25°C.

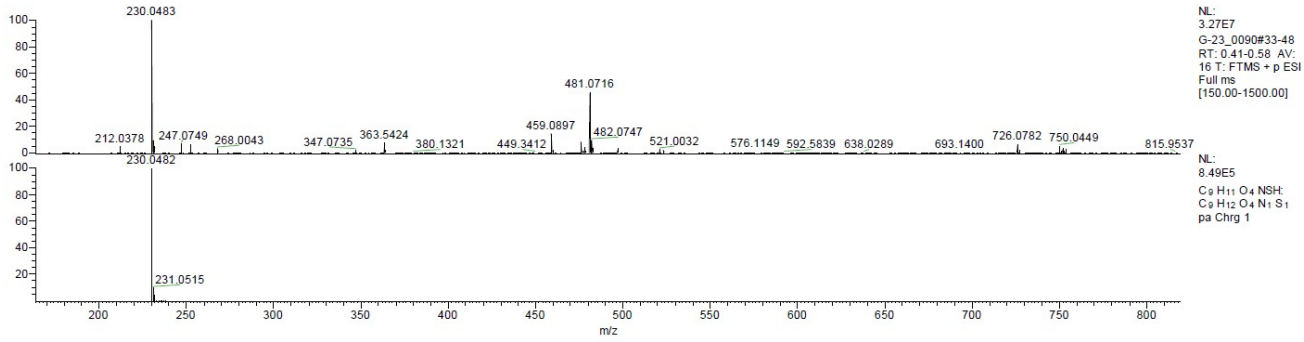


Figure S5. ESI mass spectrometry analysis of M1.

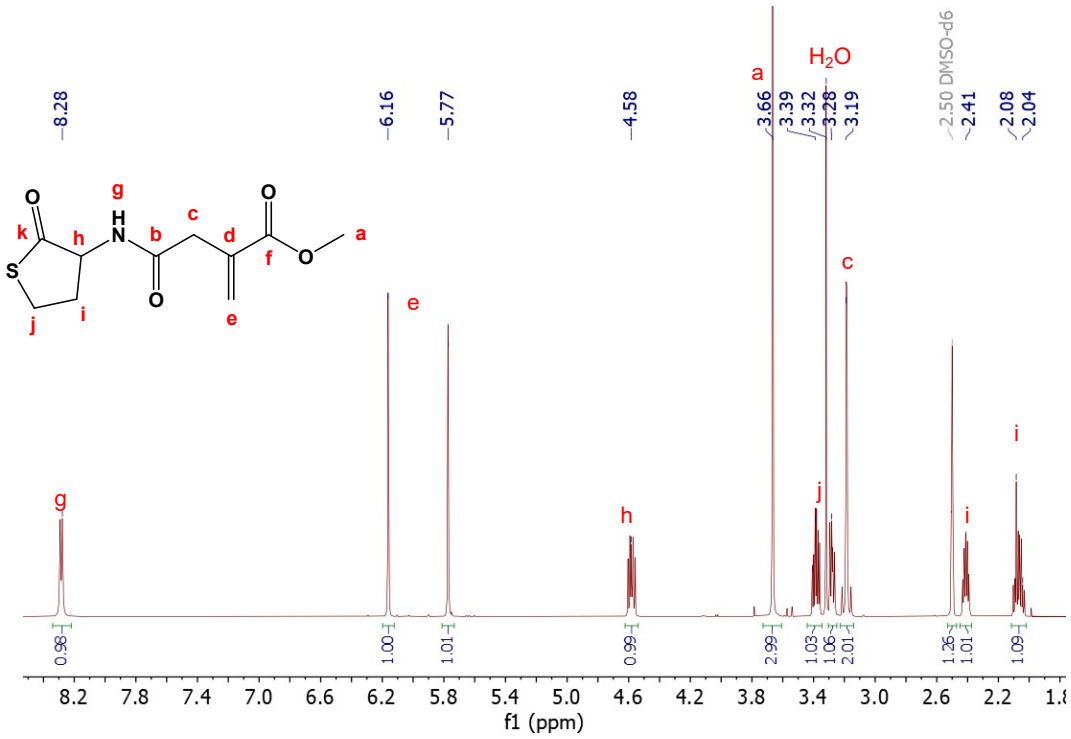


Figure S6. ^{1}H NMR spectrum of esterified monofunctional monomer M2 in DMSO-d_6 at 25°C.

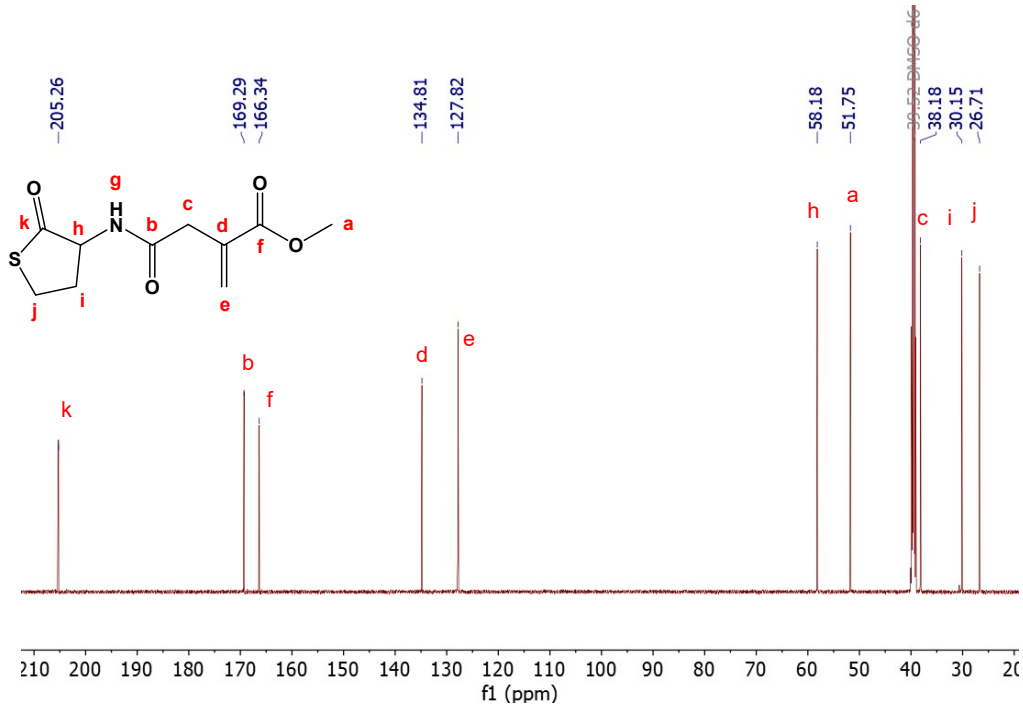


Figure S7. ^{13}C NMR spectrum of esterified monofunctional monomer M2 in DMSO-d_6 at 25°C.

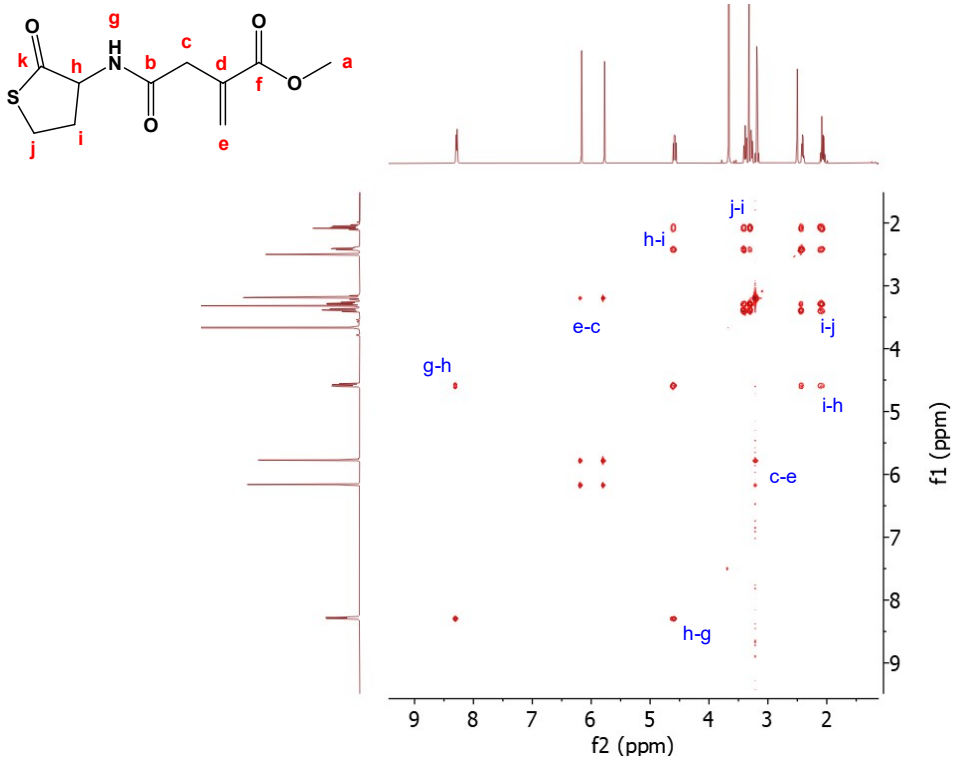


Figure S8. COSY NMR spectrum of monofunctional monomer M2 in DMSO-d_6 at 25°C.

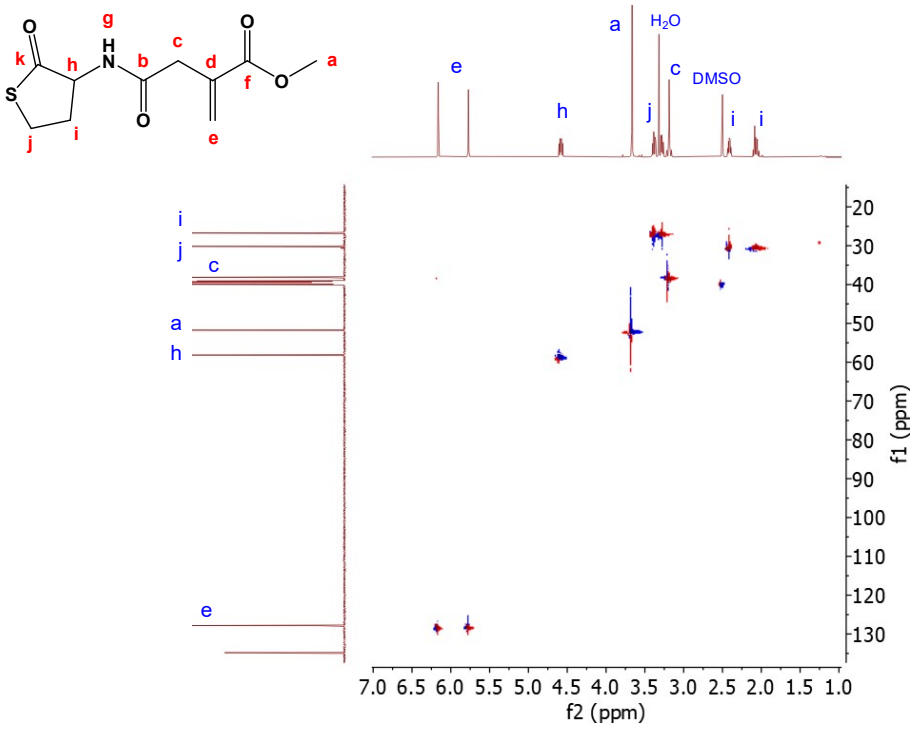


Figure S9. ^{1}H-^{13}C HSQC NMR spectrum of monofunctional monomer M2 in DMSO-d_6 at 25°C.

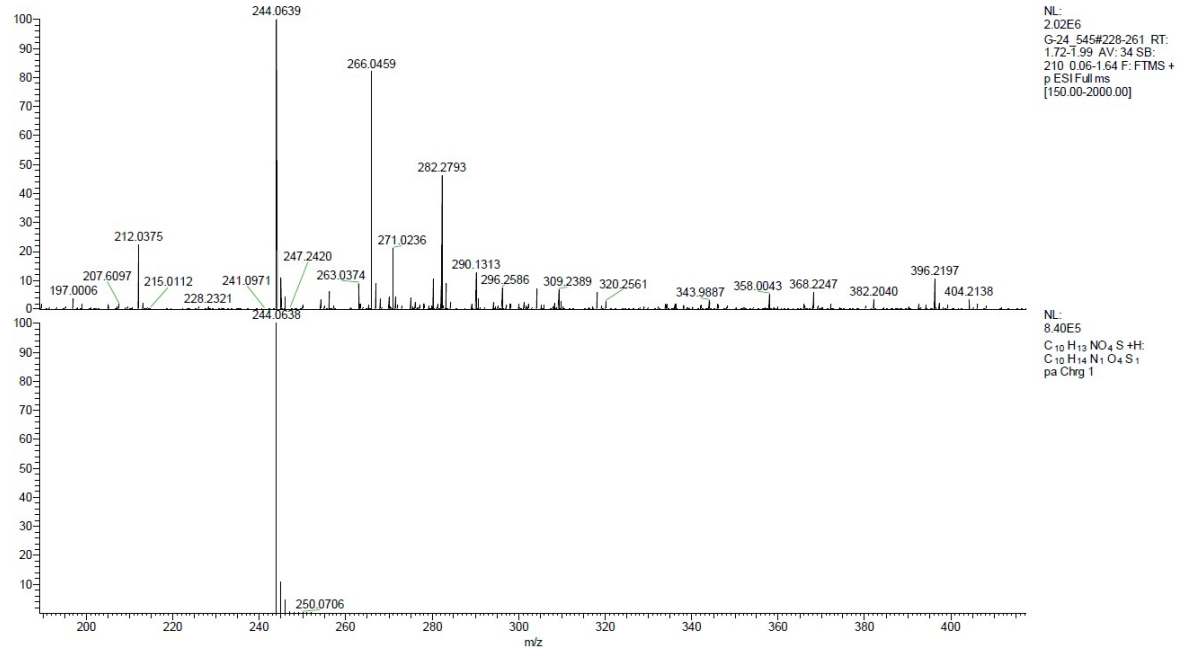
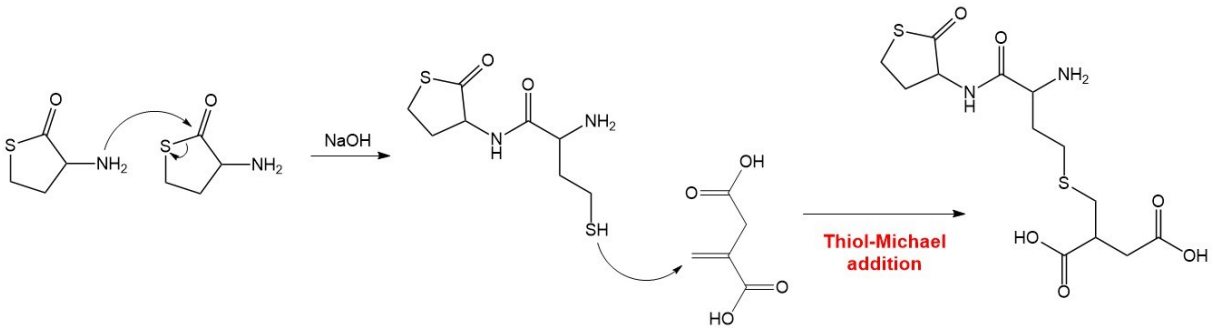


Figure S10. ESI mass spectrometry analysis of M2.



Scheme S1. Possible side-reactions during the monomer syntheses.

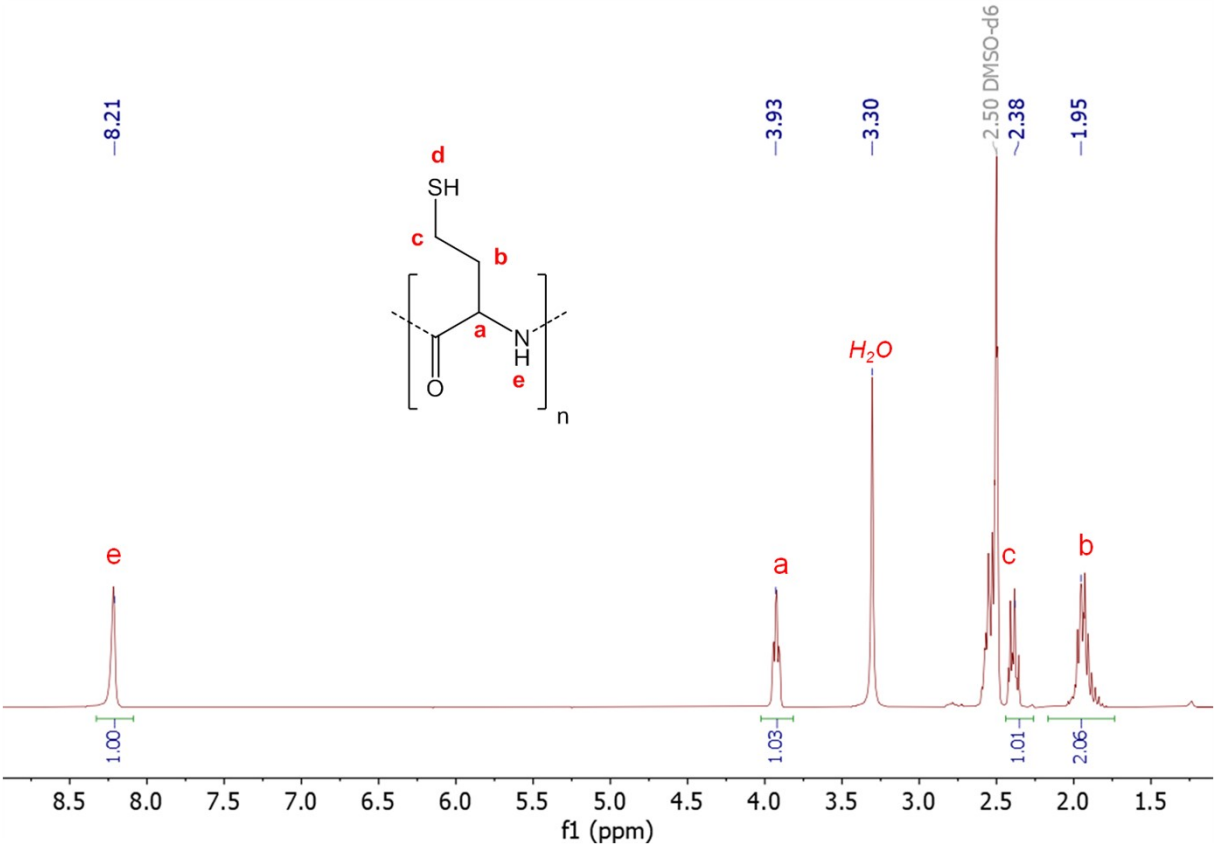


Figure S11. ^{1}H NMR spectrum in DMSO-d_6 of the polymer obtained for reaction 1 Table S1 without coupling agent.

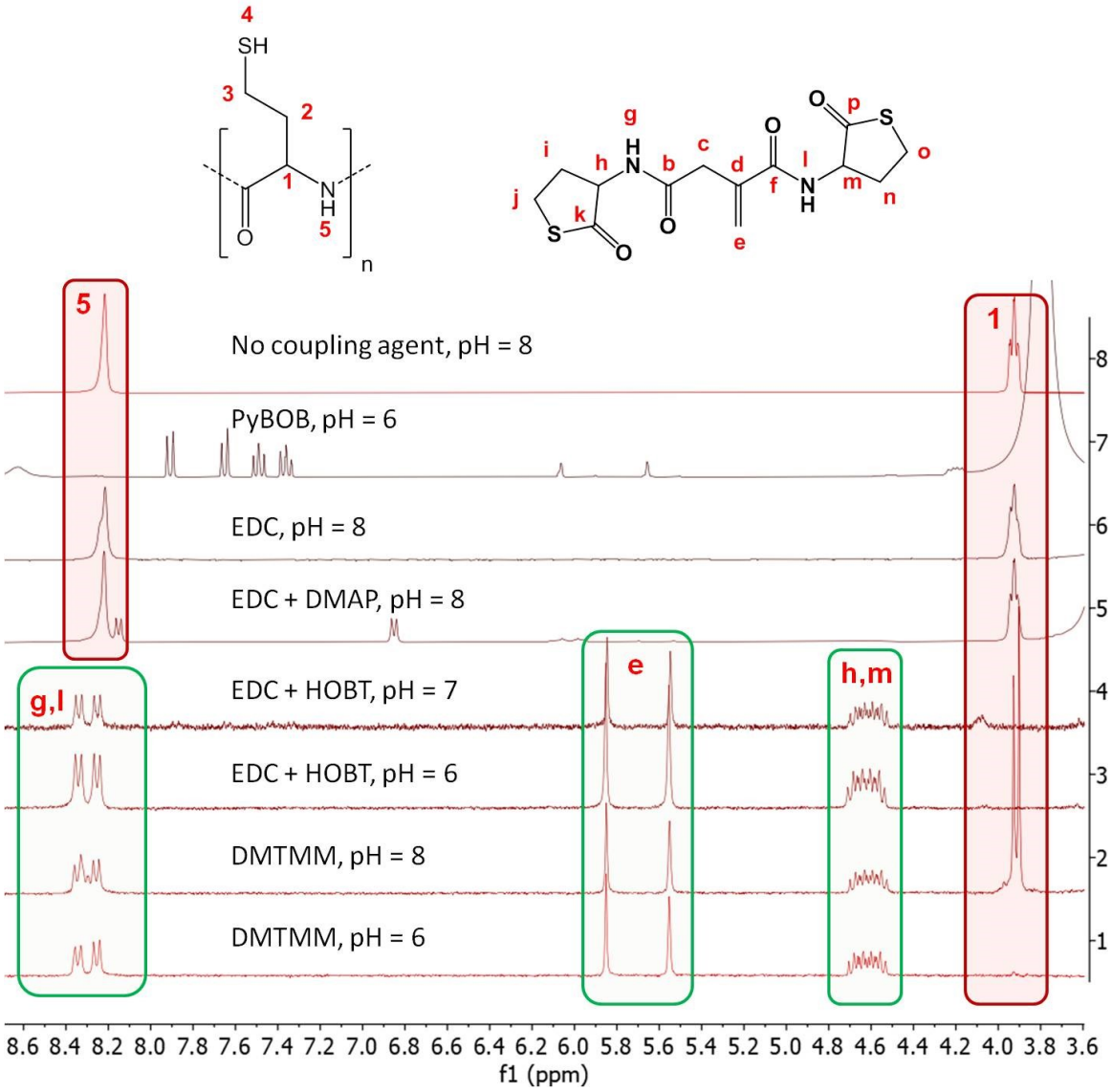


Figure S12. ^{1}H NMR spectra in DMSO-d_6 of the reaction mixtures of M3 synthesis under various conditions.

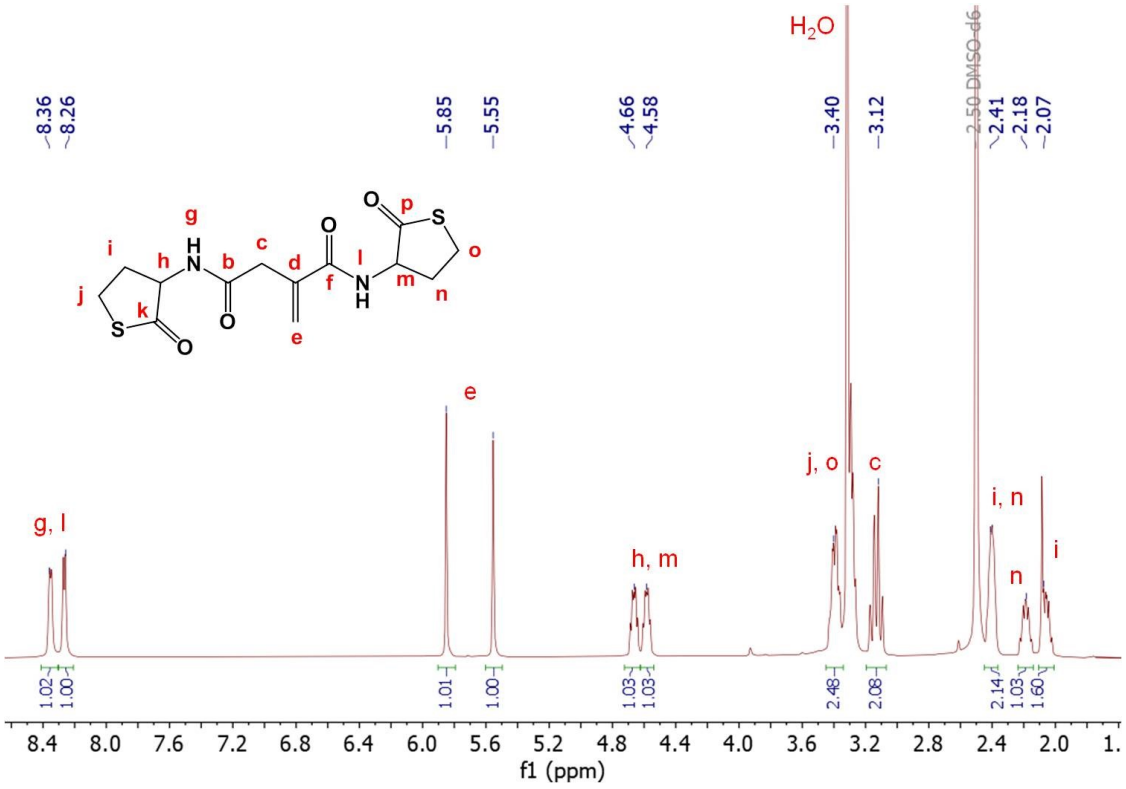


Figure S13. ^{1}H NMR spectrum of difunctional monomer M3 in DMSO-d_6 at 25°C.

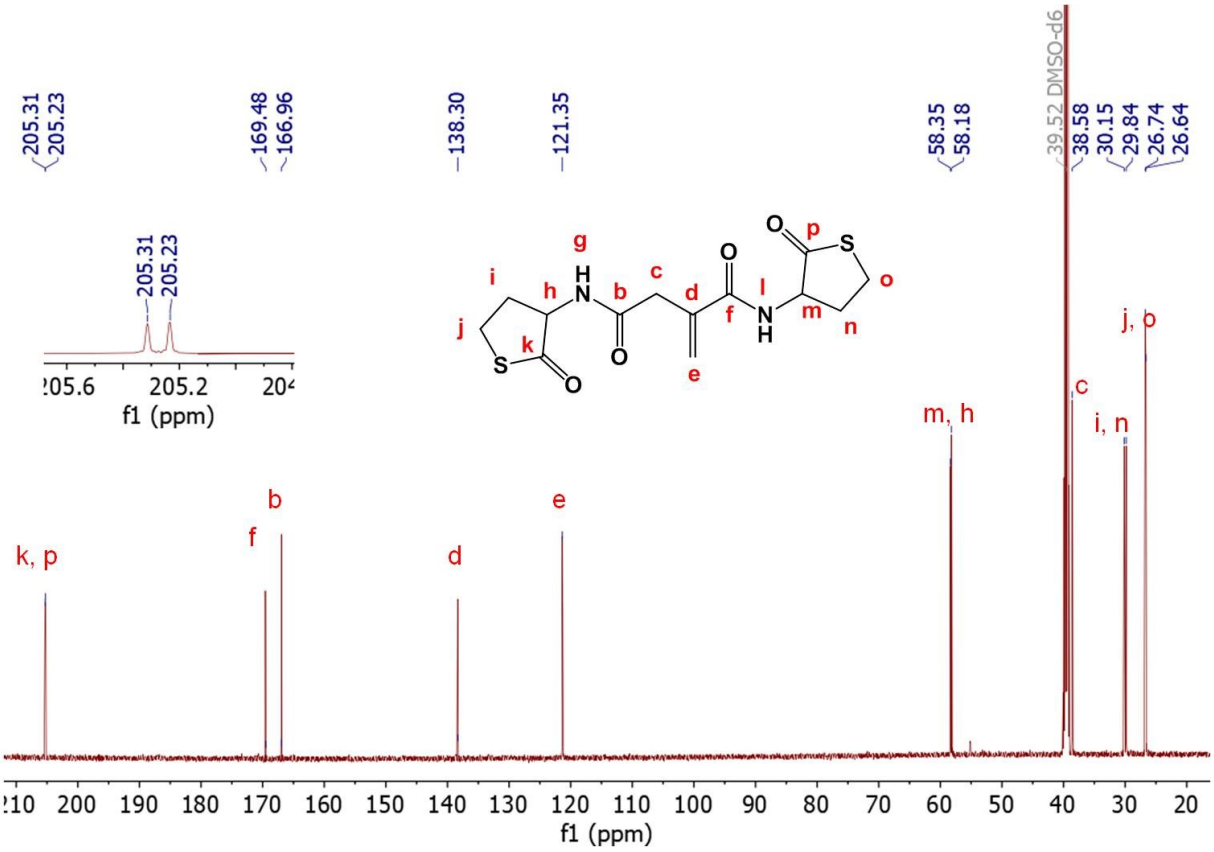


Figure S14. ^{13}C NMR spectrum of bifunctional monomer M3 in DMSO-d_6 at 25°C.

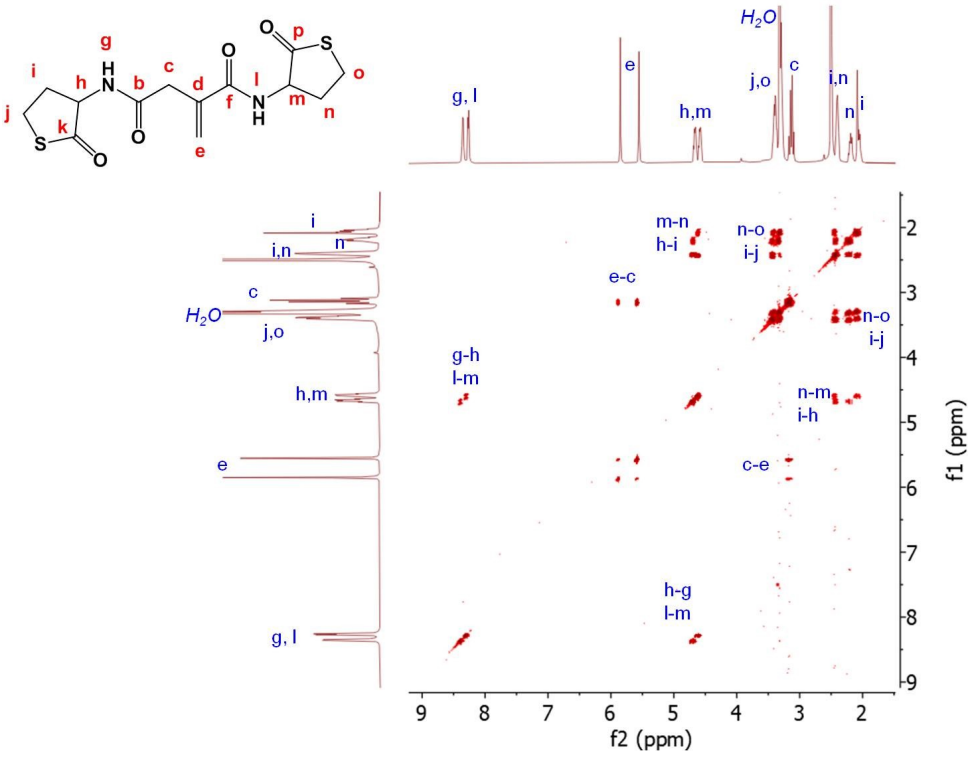


Figure S15. COSY NMR spectrum of bifunctional monomer M3 in DMSO-d_6 at 25°C.

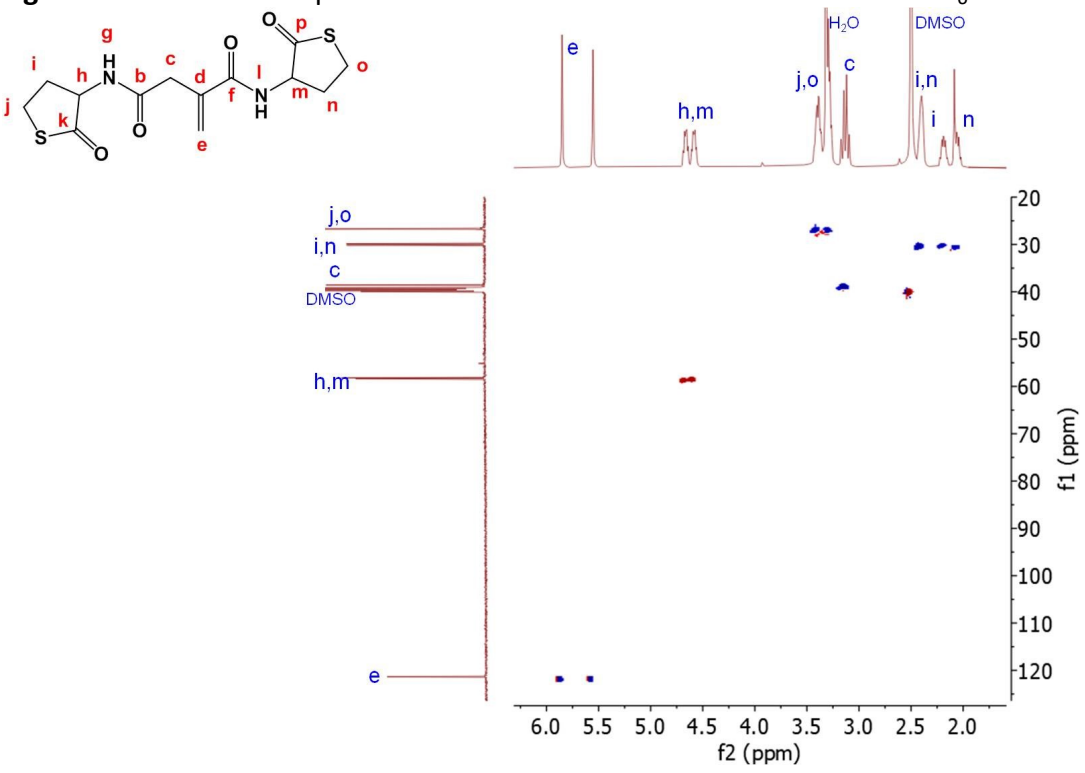


Figure S16. ^{1}H-^{13}C HSQC NMR spectrum of bifunctional monomer M3 in DMSO-d_6 at 25°C.

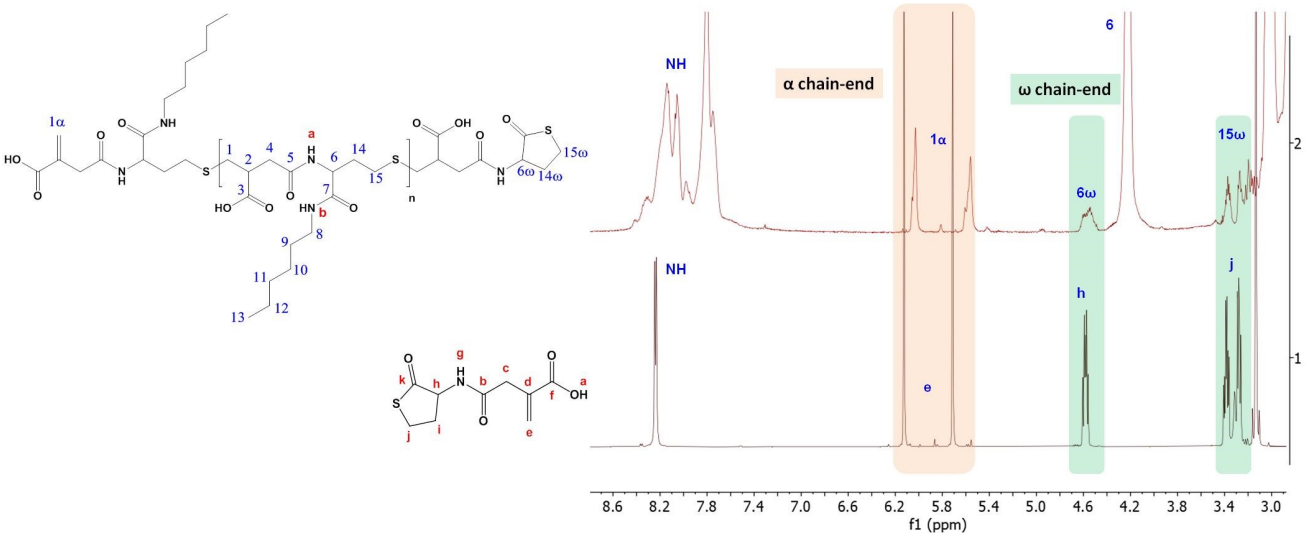


Figure S17. ^{1}H NMR spectra in DMSO-d_6 of M1 monomer and of a poly(amide-thioether) obtained in Table 1, run 1.

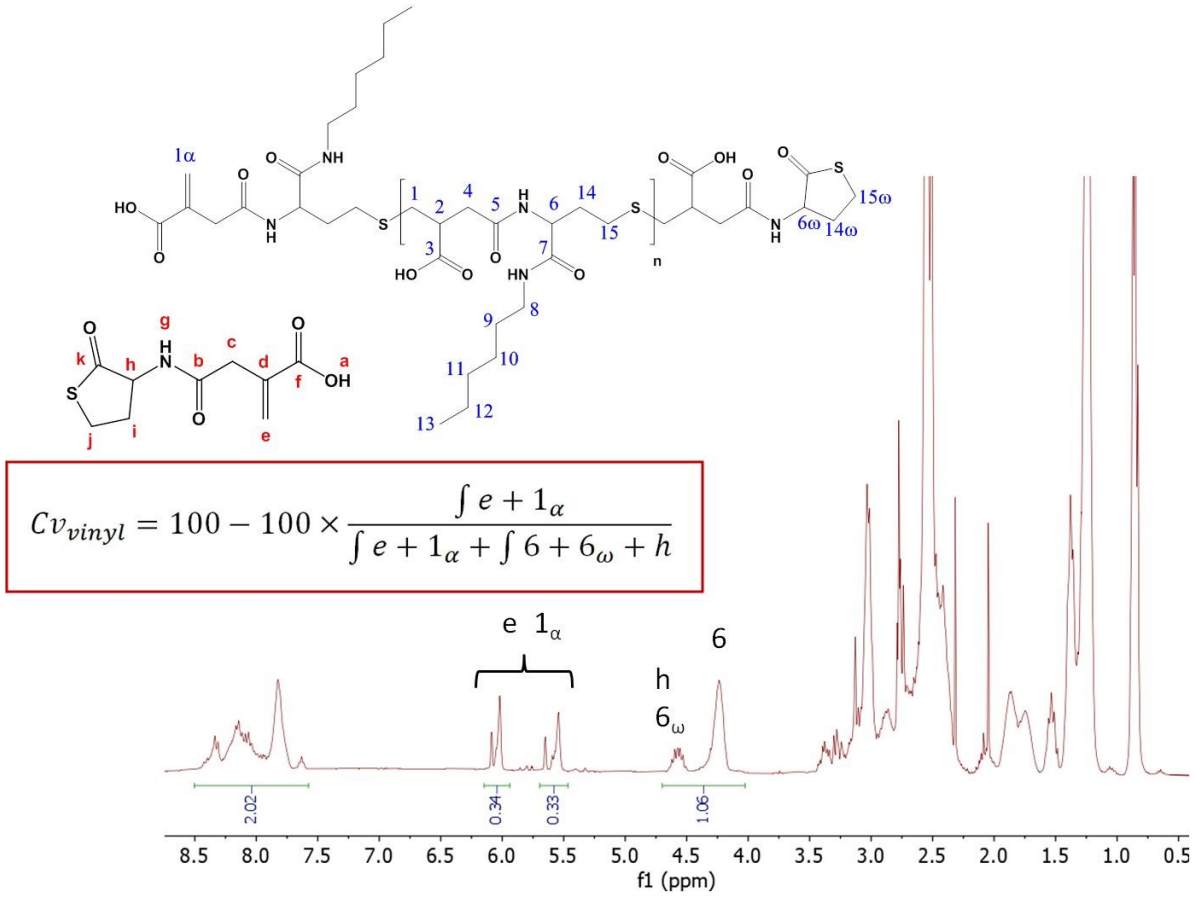


Figure S18. ^{1}H NMR spectrum in DMSO-d_6 at 25°C of the reaction mixture after 6 h of the synthesis of a poly(amide-thioether) by the reaction of M1 with *n*-hexylamine (Table 1, run1).

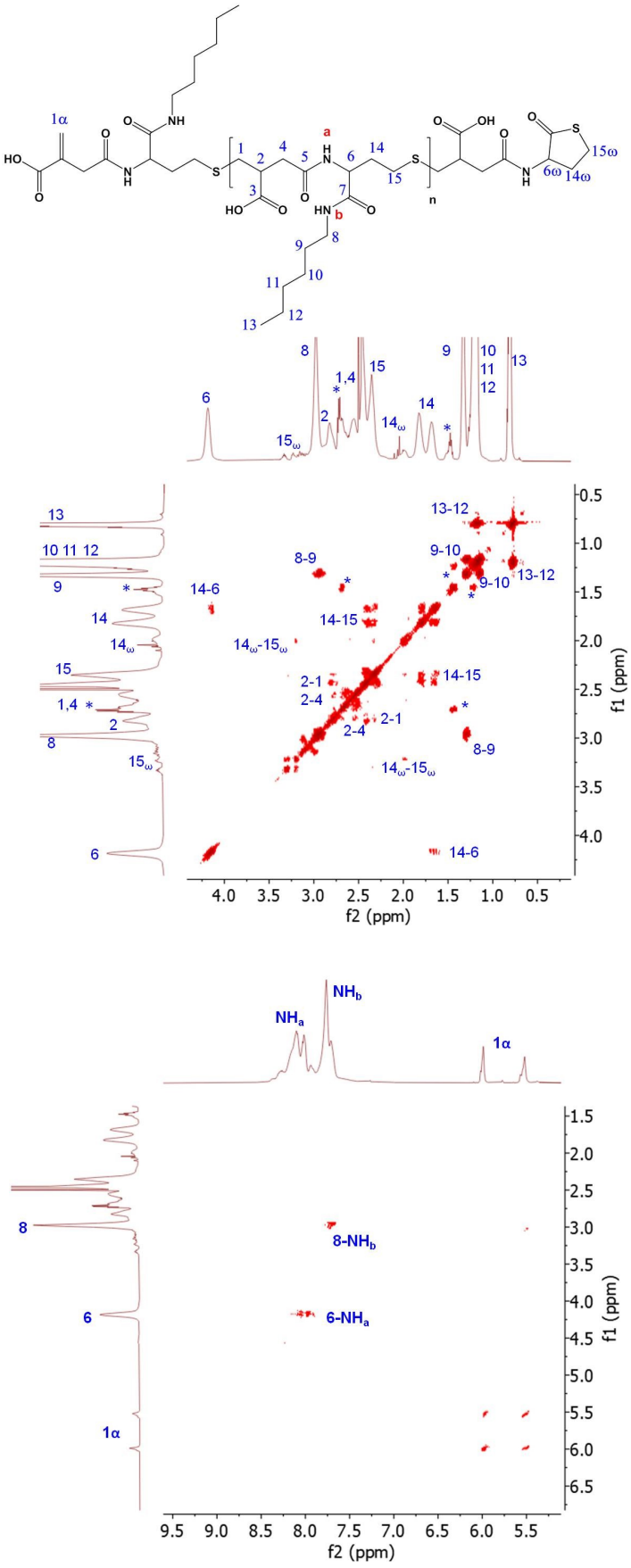


Figure S19. ^{1}H-^{1}H COSY NMR spectrum in DMSO-d_6 at 25°C of a poly(amide-thioether) synthesized by the reaction of M1 with *n*-hexylamine (Table 1, run1).

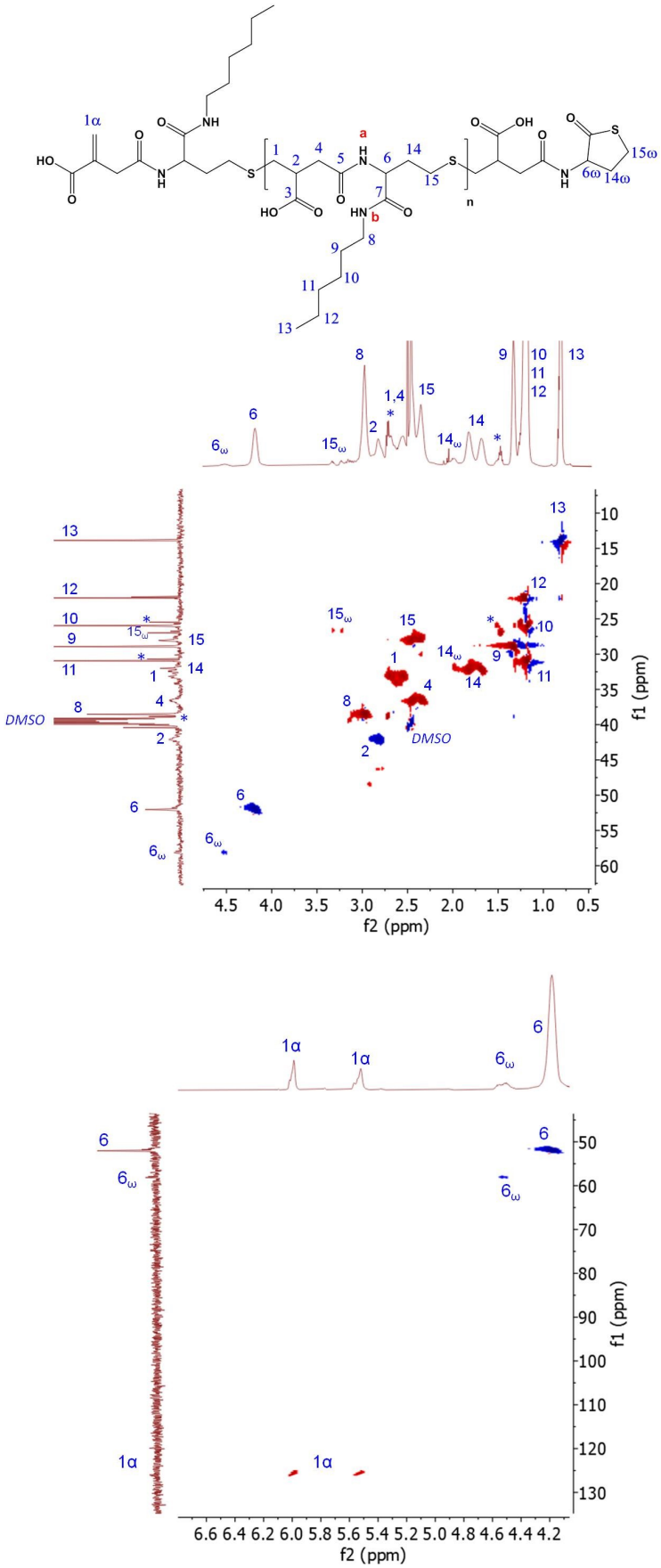


Figure S20. ^{1}H-^{13}C HSQC NMR spectrum in DMSO-d_6 at 25°C of a poly(amide-thioether) synthesized by the reaction of M1 with *n*-hexylamine (Table 1, run1).

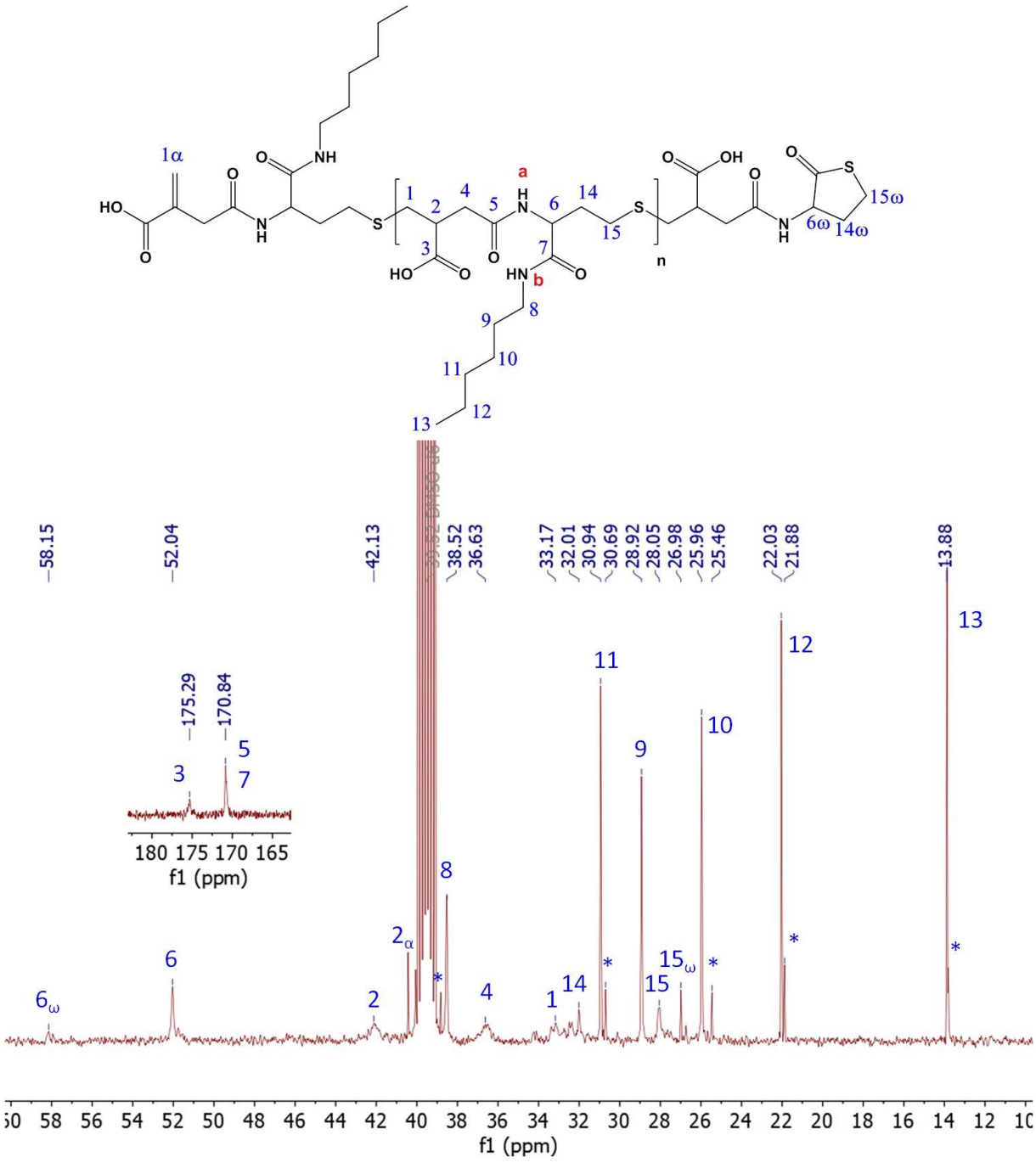


Figure S21. ^{13}C NMR spectrum in DMSO-d_6 at 25°C of a poly(amide-thioether) synthesized by the reaction of M1 with *n*-hexylamine (Table 1, run1).

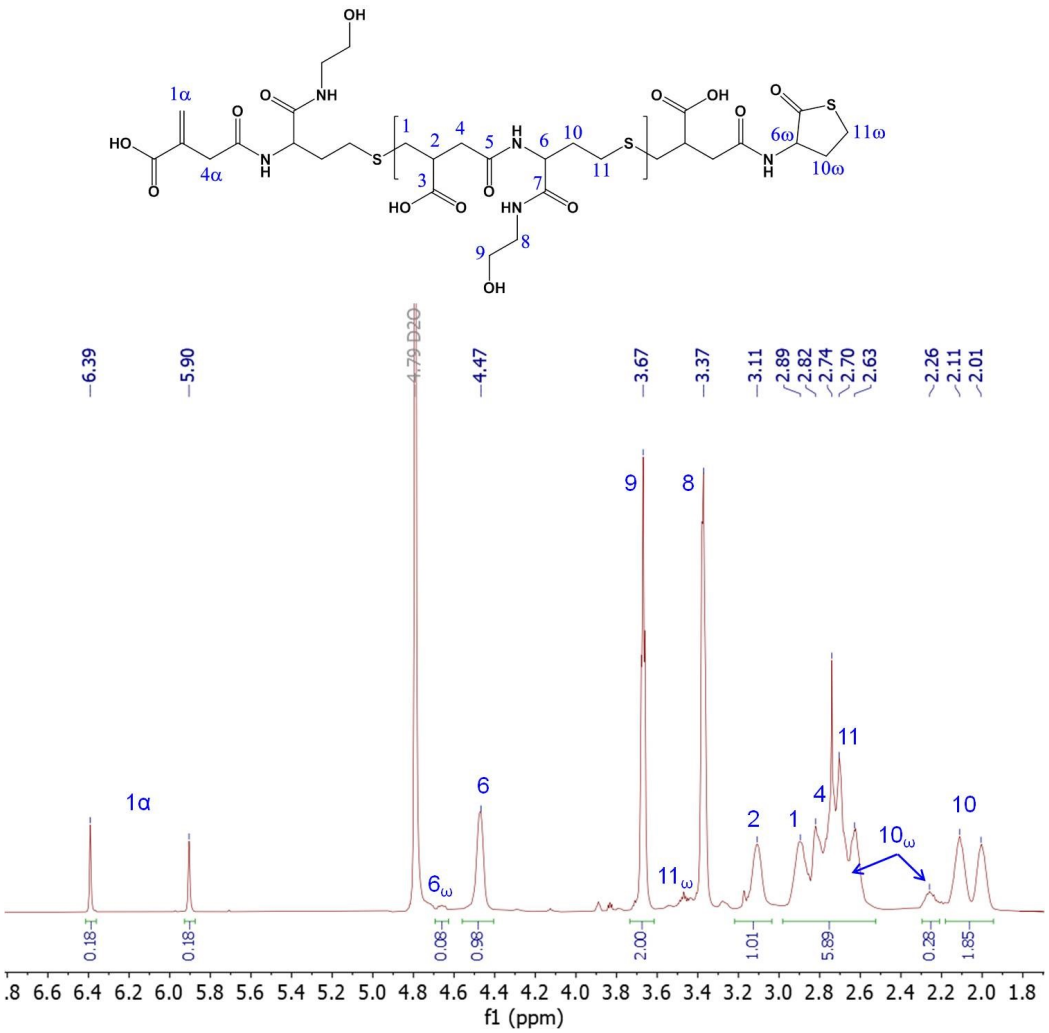


Figure S22. ^{1}H NMR spectrum in D_2O at 25°C of a poly(amide-thioether) synthesized by the reaction of M1 with ethanolamine (Table 1, run 6).

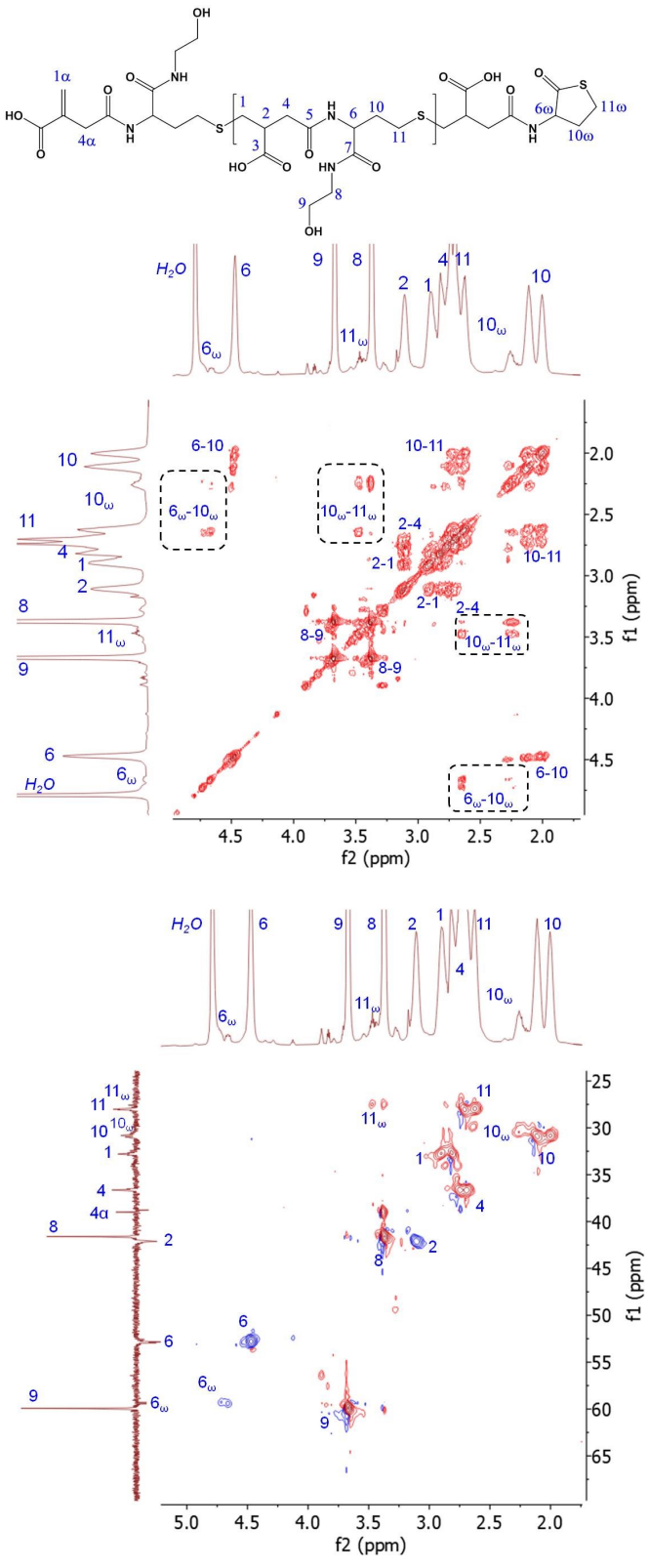


Figure S23. ^{1}H-^{1}H COSY NMR spectrum in D_2O at 25°C of a poly(amide-thioether) synthesized by the reaction of M1 with ethanolamine (Table 1, run 6).

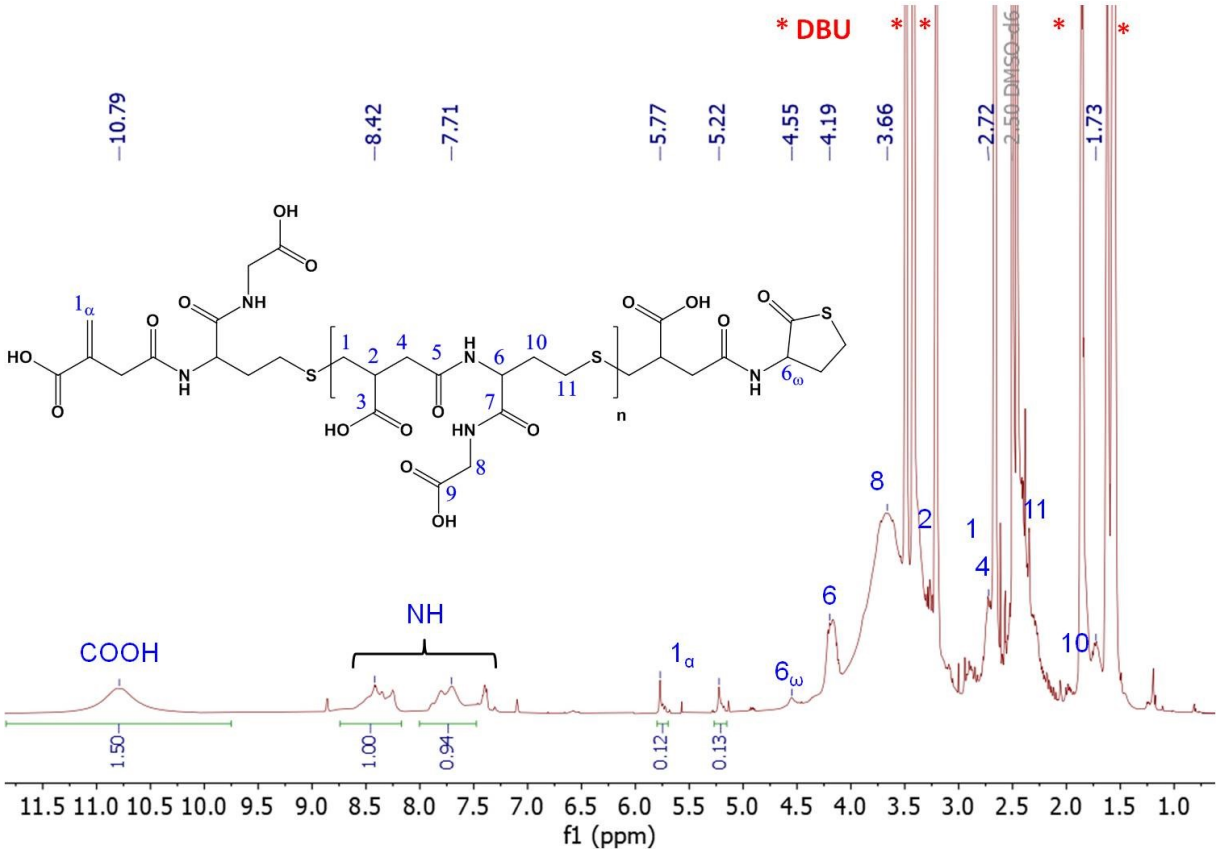


Figure S24. ^{1}H NMR spectrum in DMSO-d_6 at 25°C of a poly(amide-thioether) synthesized by the reaction of M1 with glycine (Table 1, run 8).

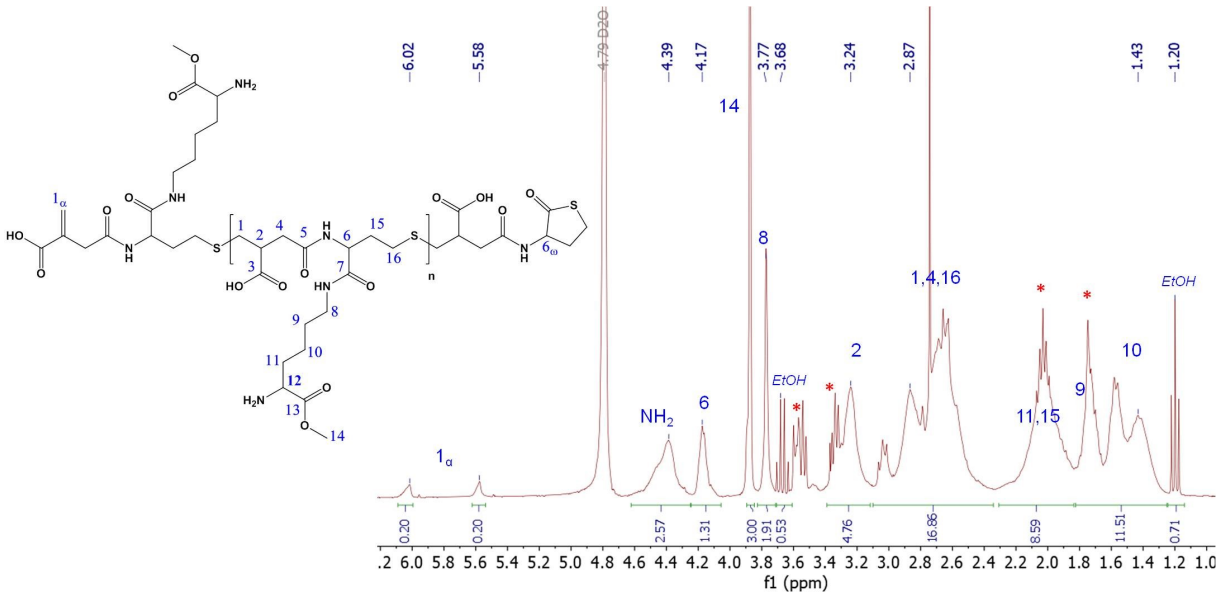


Figure S25. ^{1}H NMR spectrum in D_2O at 25°C of a poly(amide-thioether) synthesized by the reaction of M1 with L-lysine methylester (Table 1, run 9).

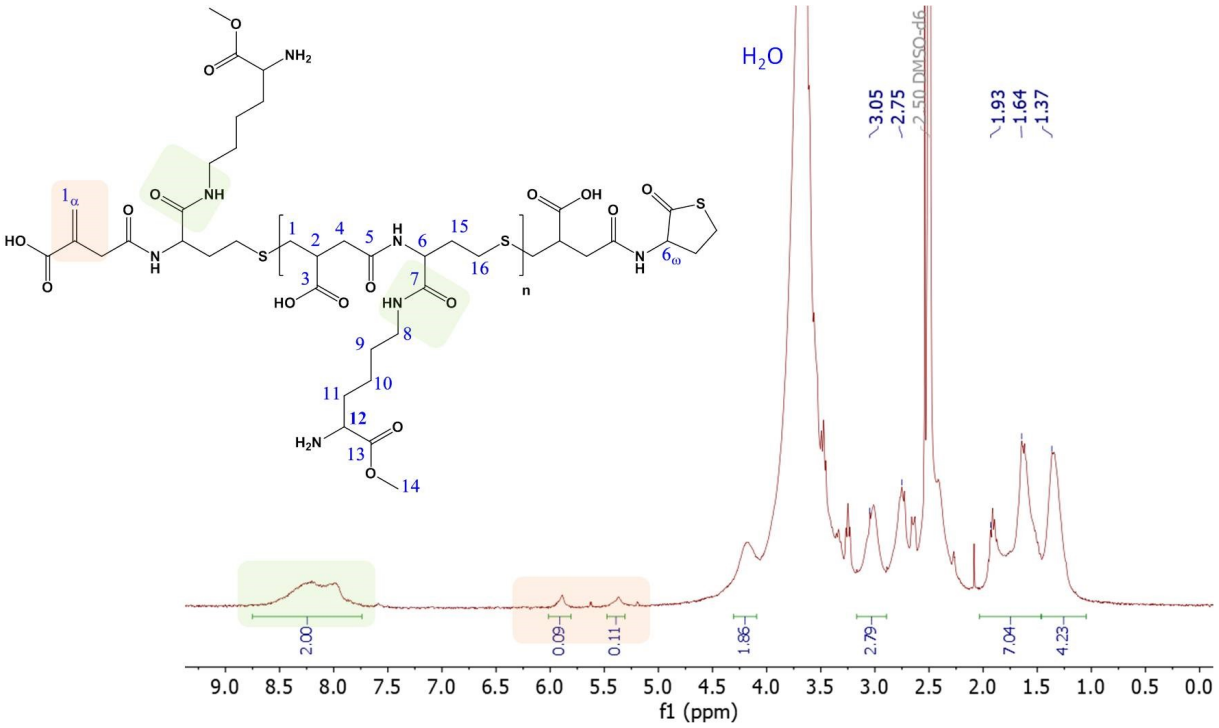


Figure S26. ^{1}H NMR spectrum in DMSO-d6 at 25°C of a poly(amide-thioether) synthesized by the reaction of M1 with L-lysine methylester (Table 1, run 9).

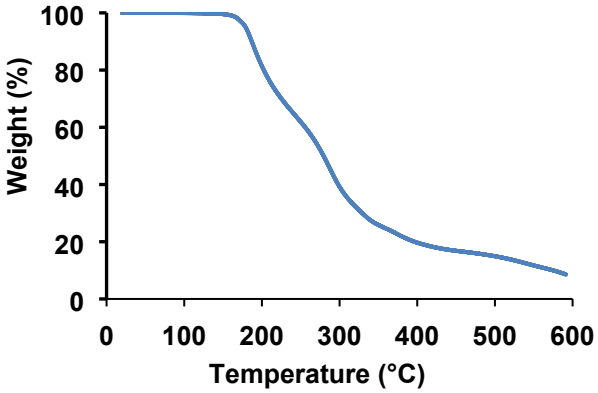
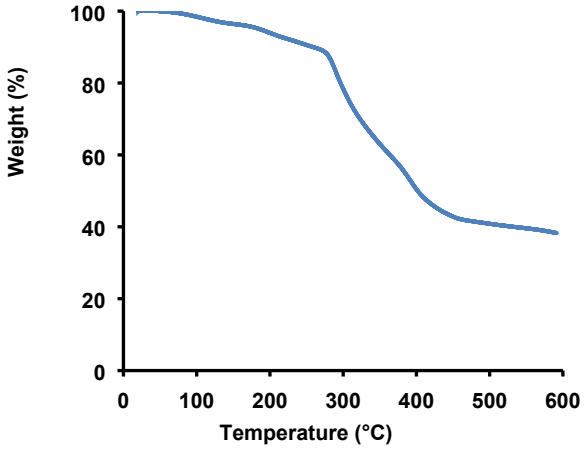


Figure S27. TGA profile for M1 monomer.

(A)



(B)

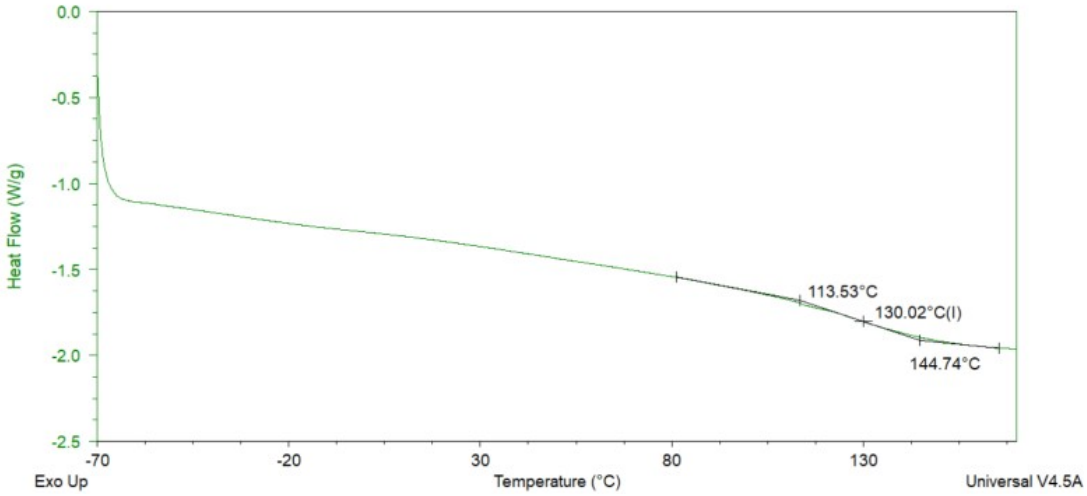


Figure S28. (A) TGA and (B) DSC thermograms for PR1, 2nd heating.

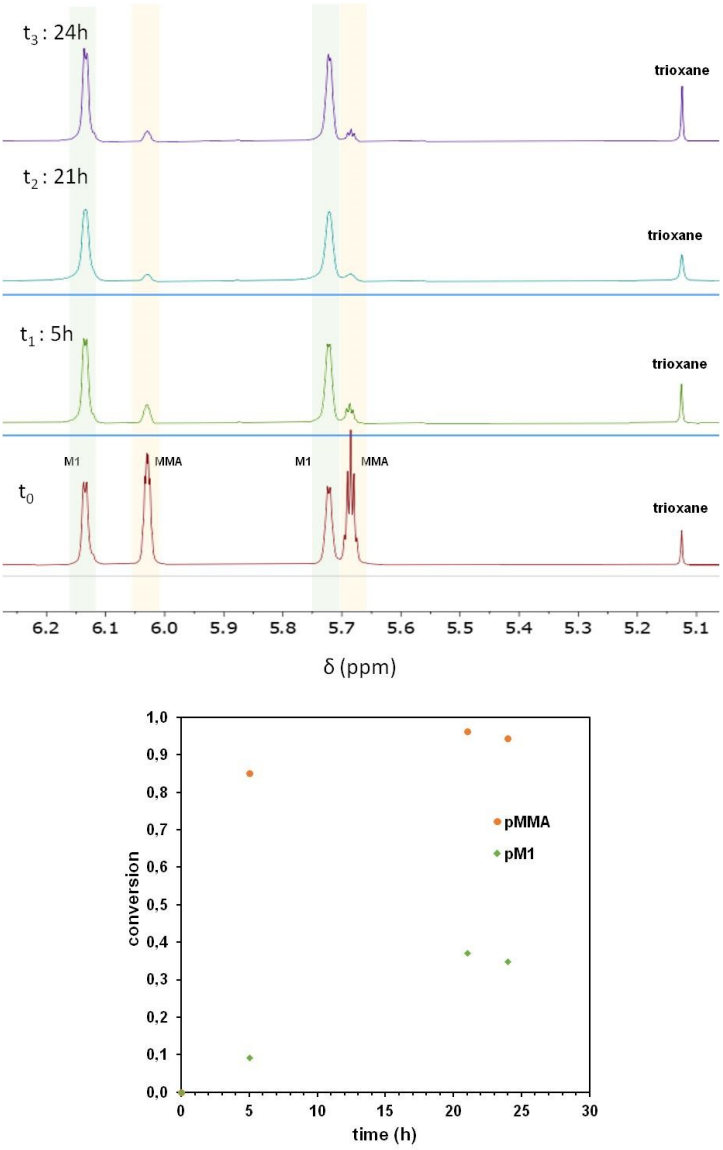


Figure S29. ^{1}H NMR overlay of aliquots from CPR1 reaction mixture (top) and individual plot of conversion over time (bottom).

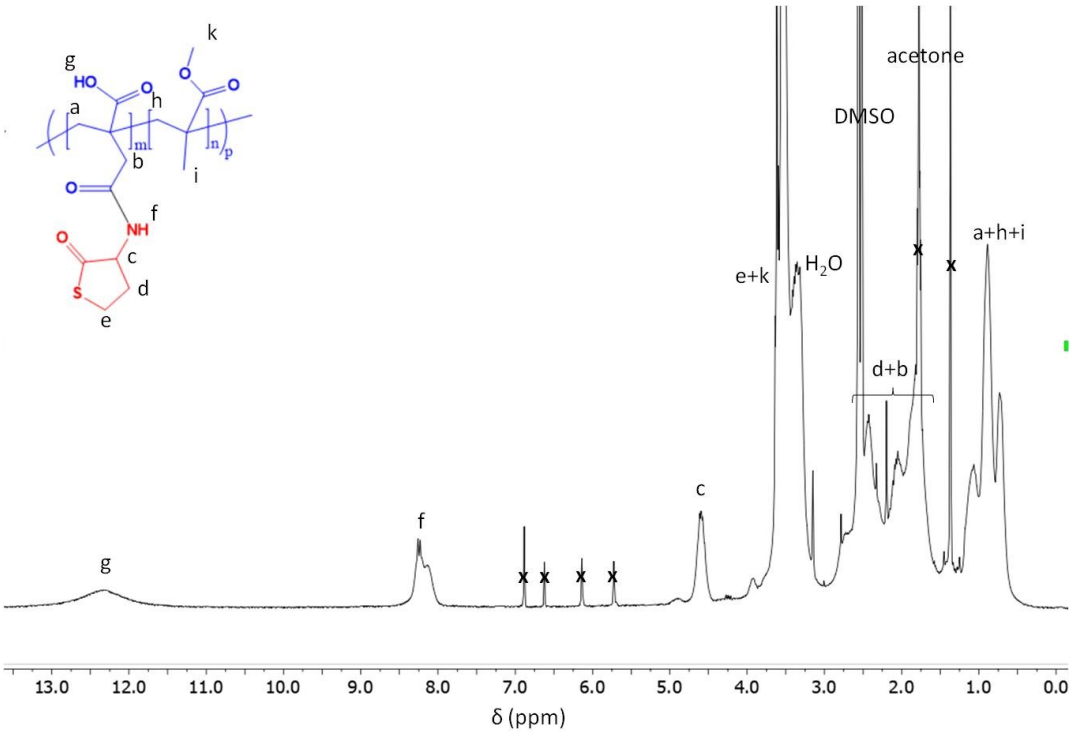


Figure S30. ^{1}H NMR spectrum in DMSO-d_6 at 25°C of the copolymer obtained by the copolymerization of M1 with MMA in Table 3, CPR1.

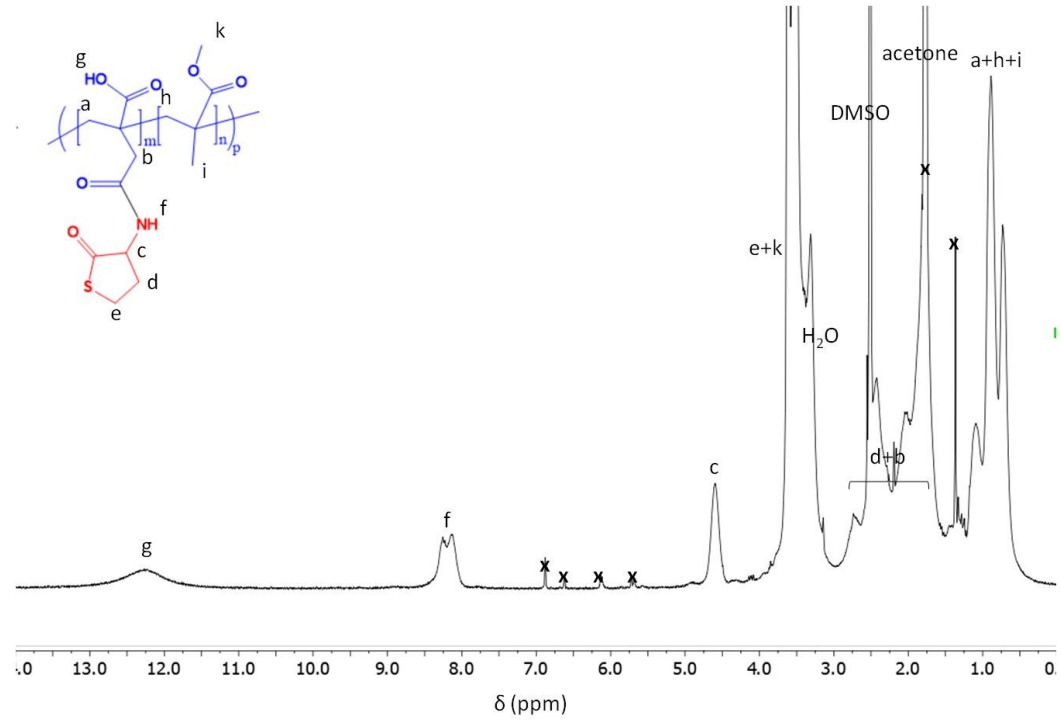


Figure S31. ^{1}H NMR spectrum in DMSO-d_6 at 25°C of the copolymer obtained by the copolymerization of M1 with MMA in Table 3, CPR2.

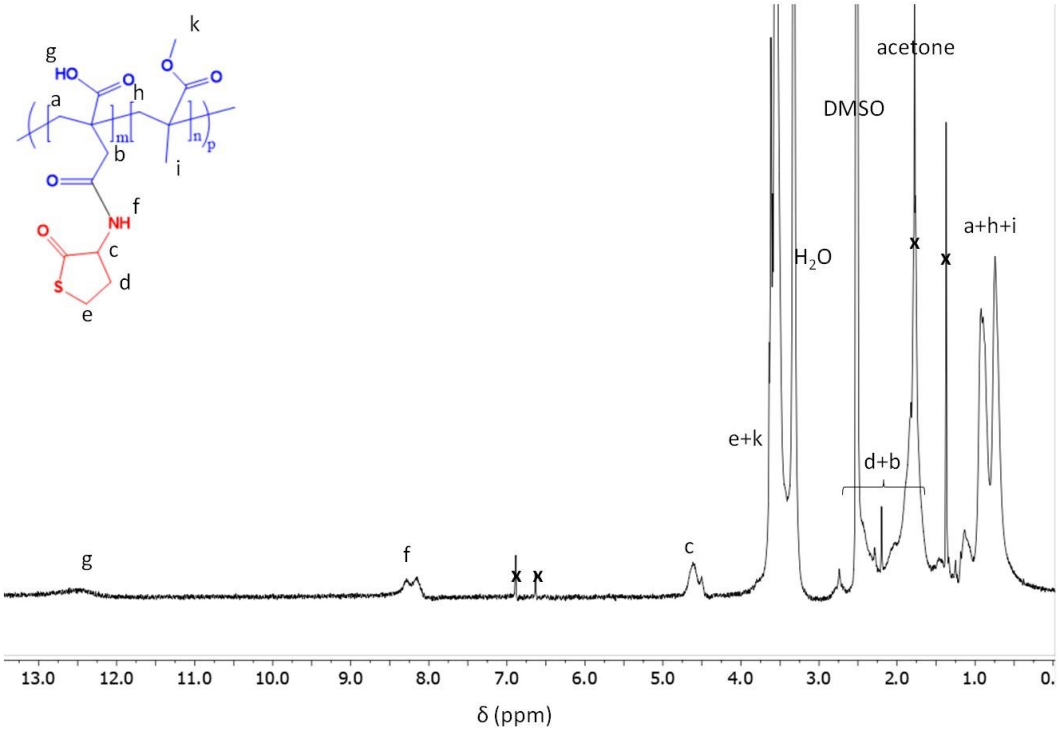


Figure S32. ^{1}H NMR spectrum in DMSO-d_6 of the copolymer obtained by the copolymerization of M1 with MMA in Table 3, CPR3.

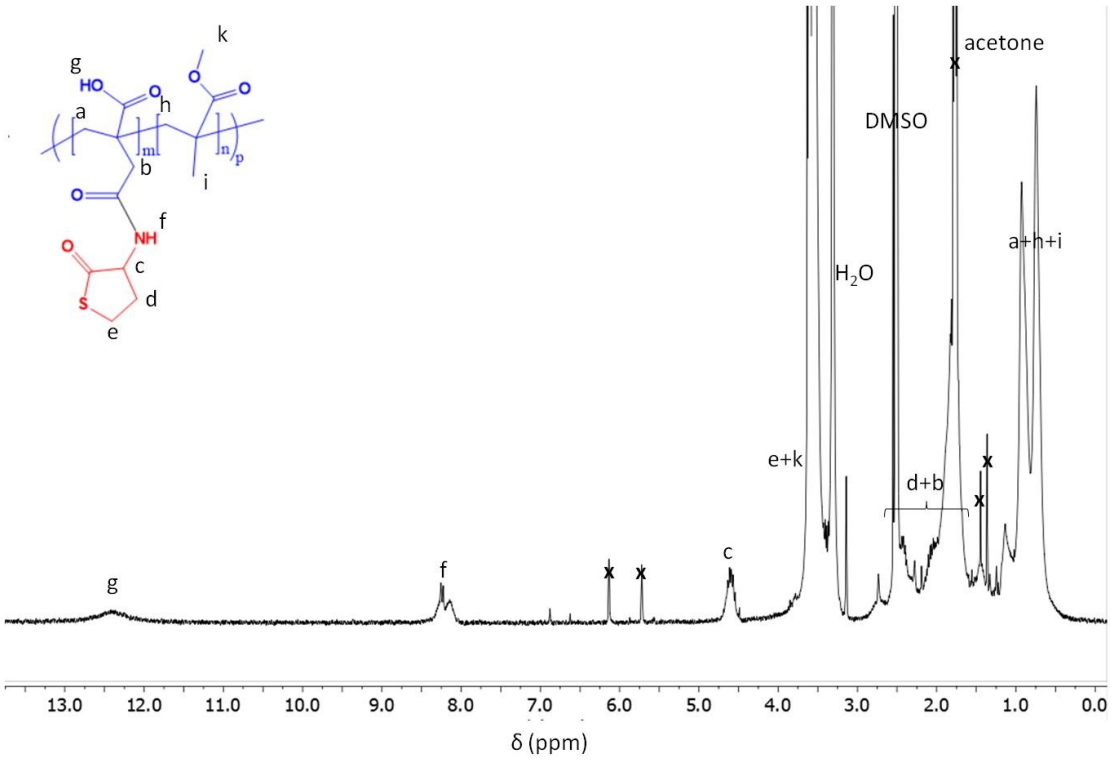


Figure S33. ^{1}H NMR spectrum in DMSO-d_6 of the copolymer obtained by the copolymerization of M1 with MMA in Table 3, CPR4.

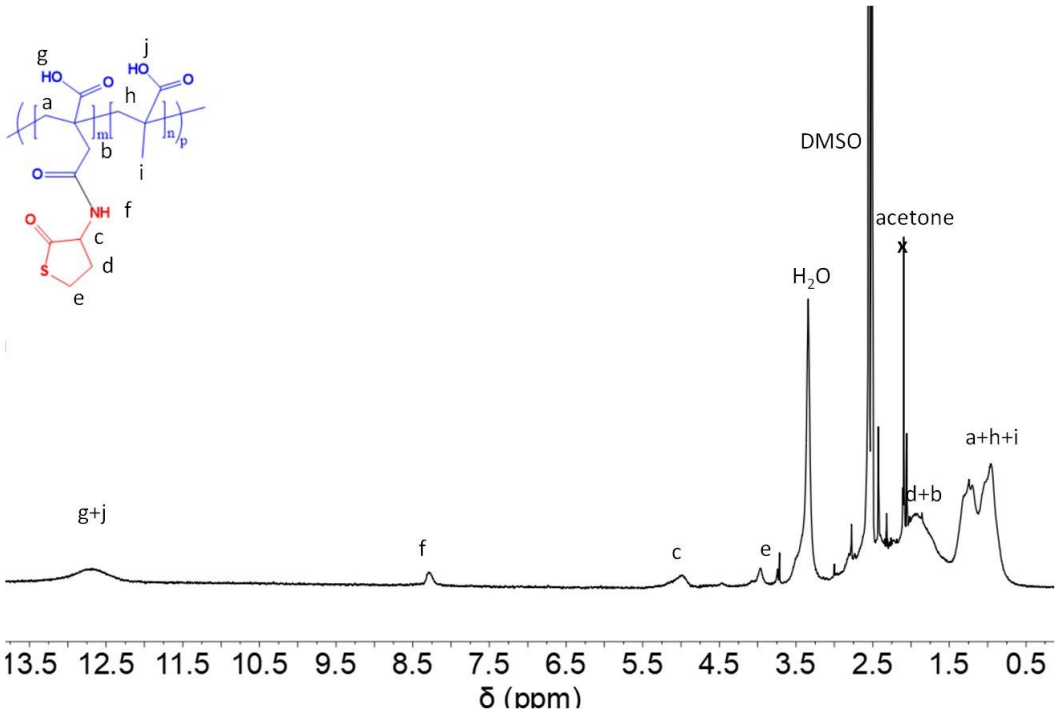


Figure S34. ^{1}H NMR spectrum in DMSO-d_6 of the copolymer obtained by the copolymerization of M1 with MMA in Table 3, CPR5.

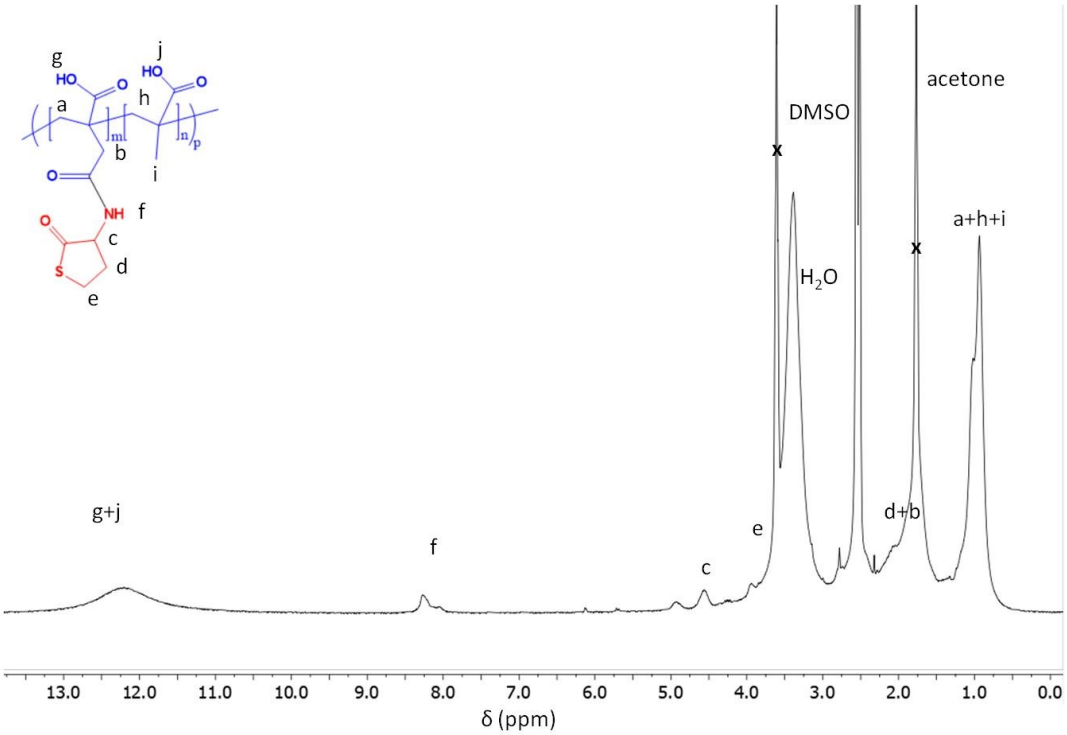


Figure S35. ^{1}H NMR spectrum in DMSO-d_6 of the copolymer obtained by the copolymerization of M1 with MAA in Table 3, CPR6.

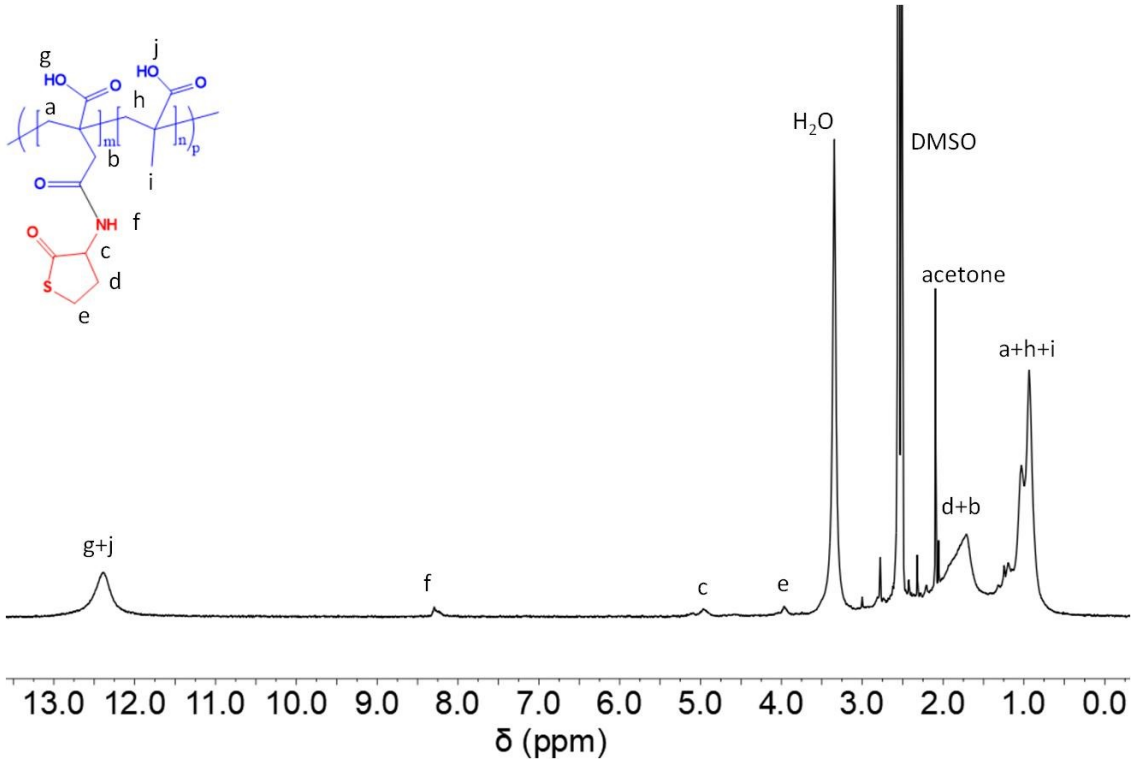


Figure S36. ^{1}H NMR spectrum in DMSO-d_6 of the copolymer obtained by the copolymerization of M1 with MAA in Table 3, CPR7.

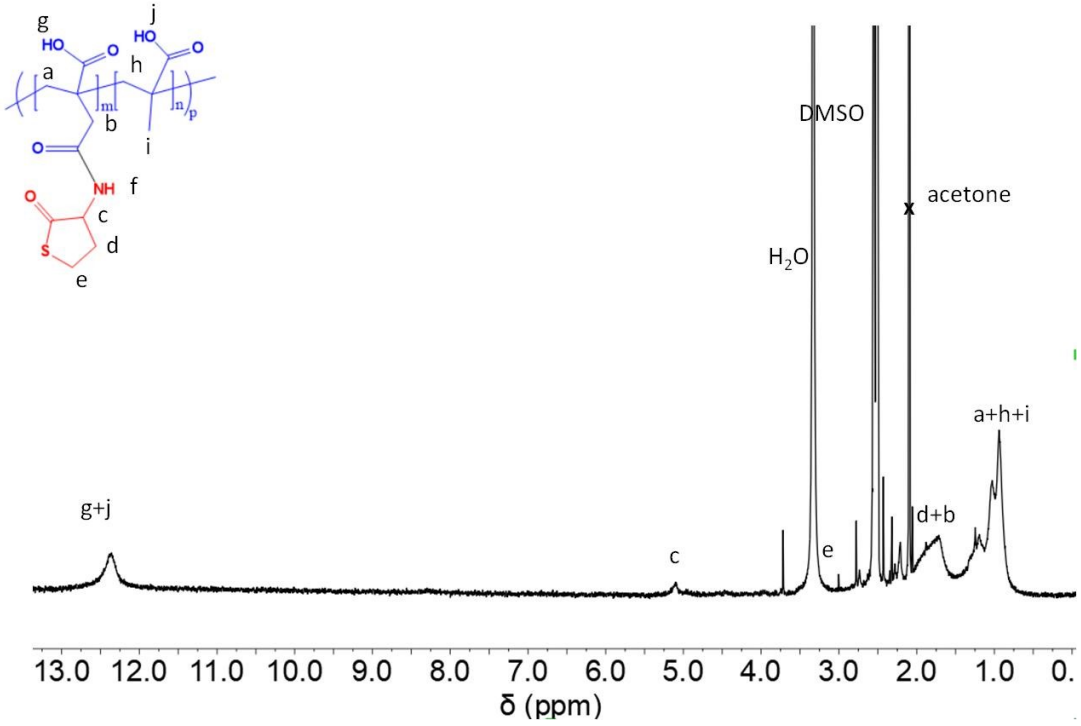


Figure S37. ^{1}H NMR spectrum in DMSO-d_6 of the copolymer obtained by the copolymerization of M1 with MAA in Table 3, CPR8.