

Electronic supplementary information

Thiol-ene coupling reaction achievement and monitoring by “in situ” UV-irradiation NMR spectroscopy

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Content:

- I. Synthesis of PAGE by anionic ring-opening polymerization in bulk.**
- II. NMR spectra.**
- III. GPC eluograms.**
- IV. “In situ” irradiation NMR spectroscopy set-up.**

I. Synthesis of PAGE by anionic ring-opening polymerization in bulk.

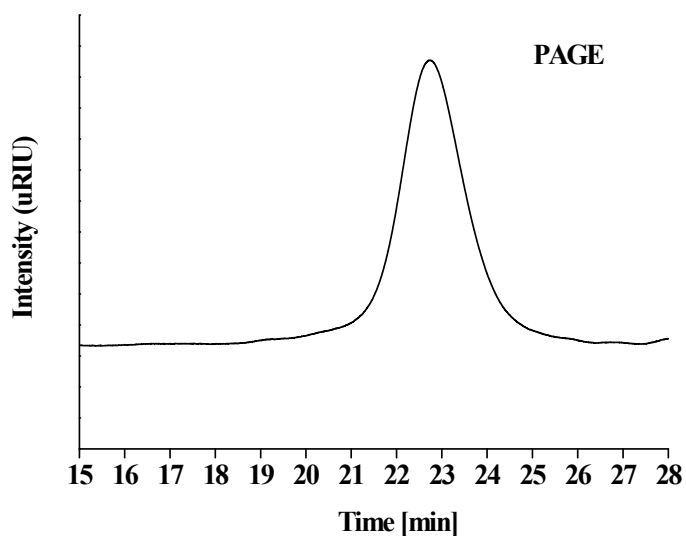


Fig. SI. 1. Chromatogram of poly(allyl glycidyl ether) (**PAGE**) precursor (RI trace, THF).

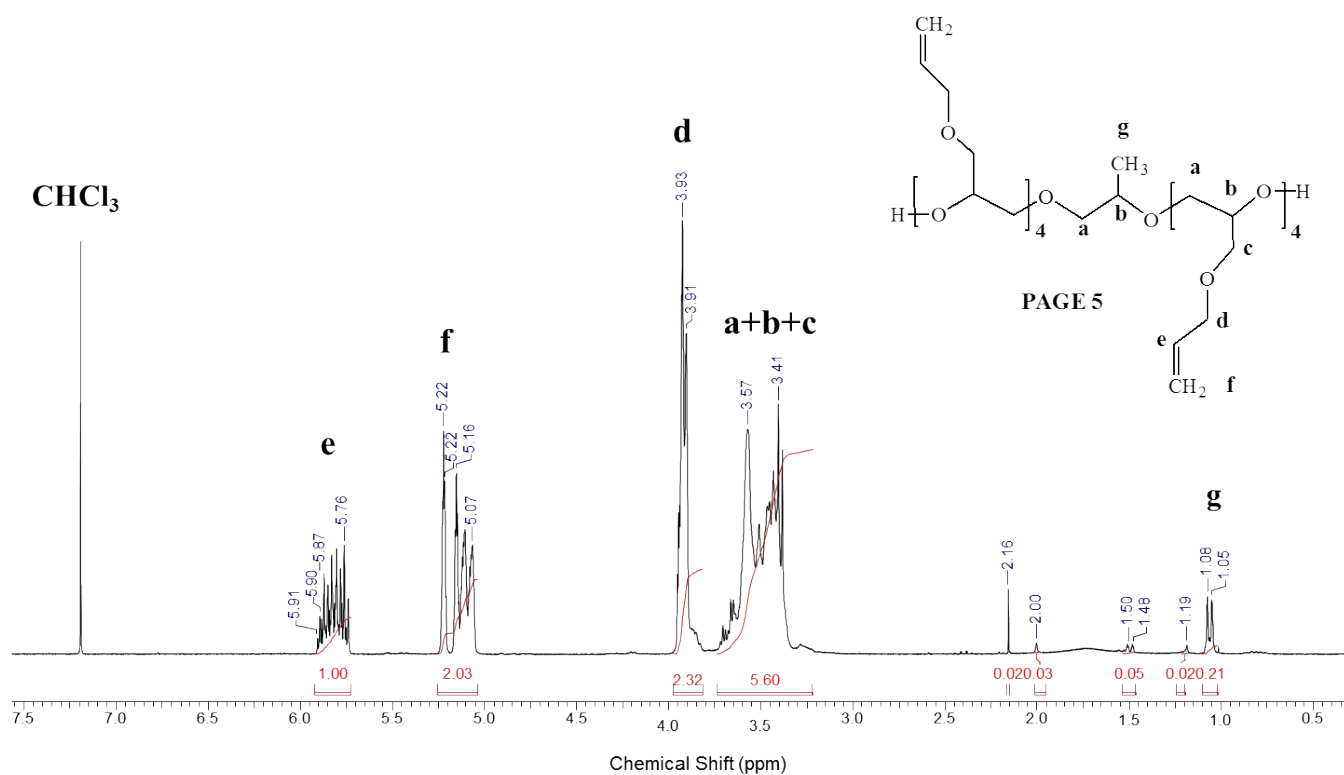


Fig. SI. 2. ¹H NMR spectrum of poly(allyl glycidyl ether) (**PAGE**) precursor in CDCl₃ (600 MHz).

II. NMR spectra.

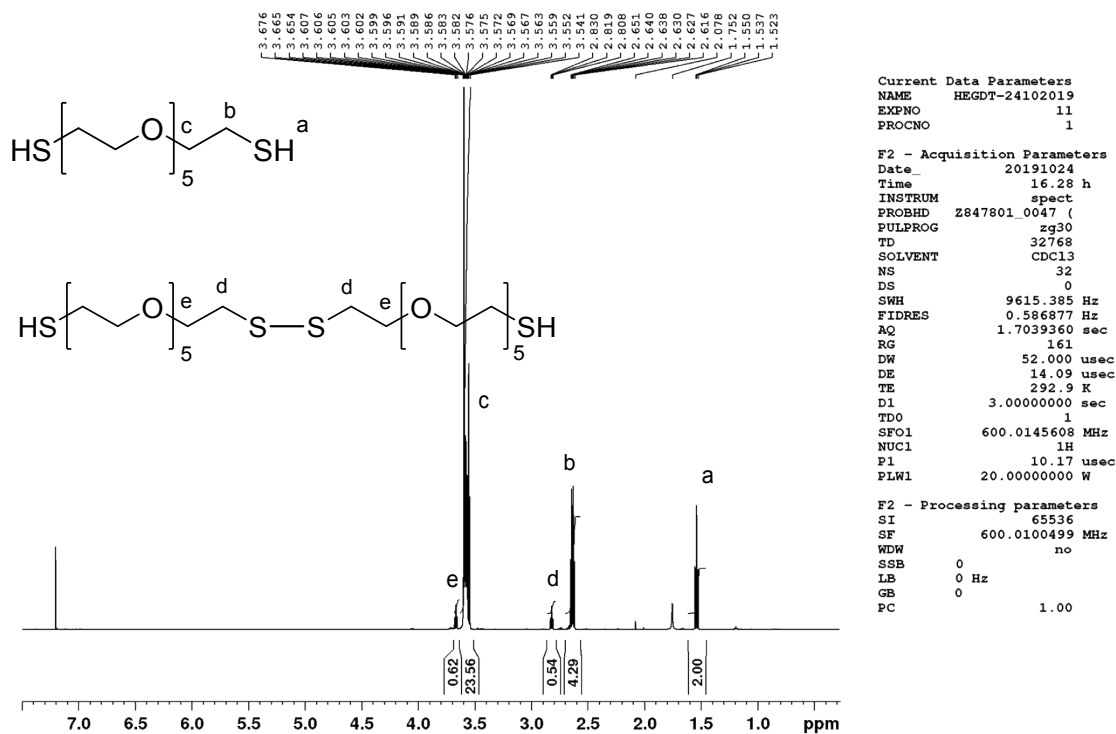


Fig. SII.1 ^1H NMR spectrum of hexa(ethylene glycol)dithiol (HEGDT) in CDCl_3 .

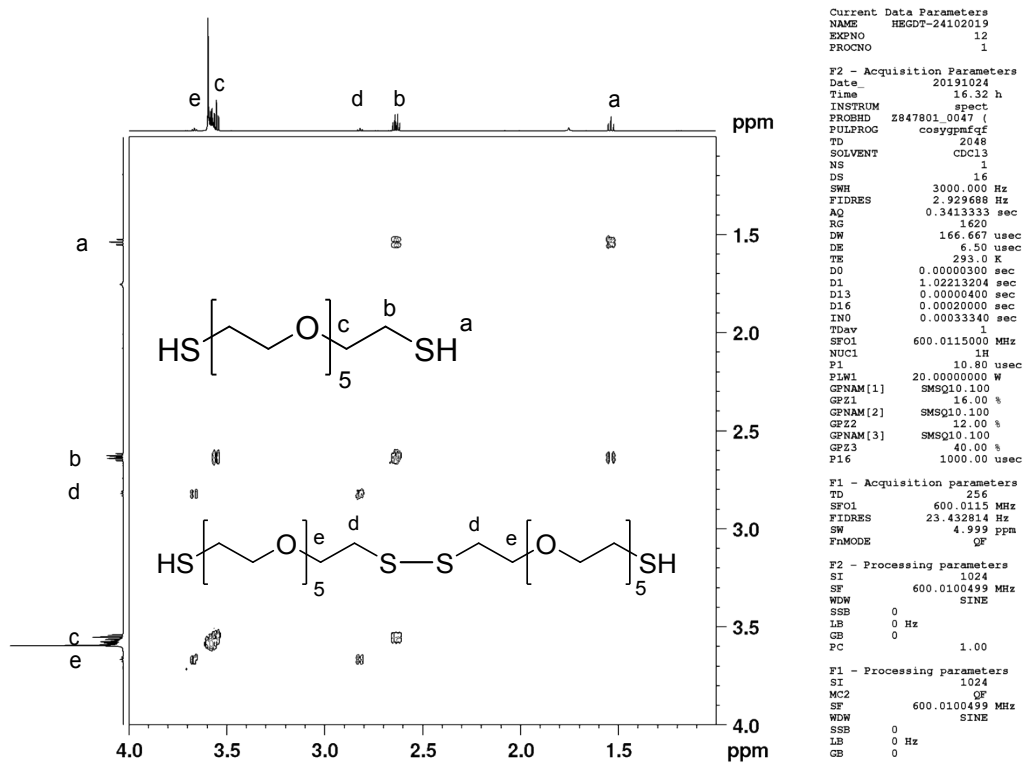


Fig. SII.2. ^1H - ^1H COSY NMR spectrum of hexa(ethylene glycol)dithiol (HEGDT) in CDCl_3 .

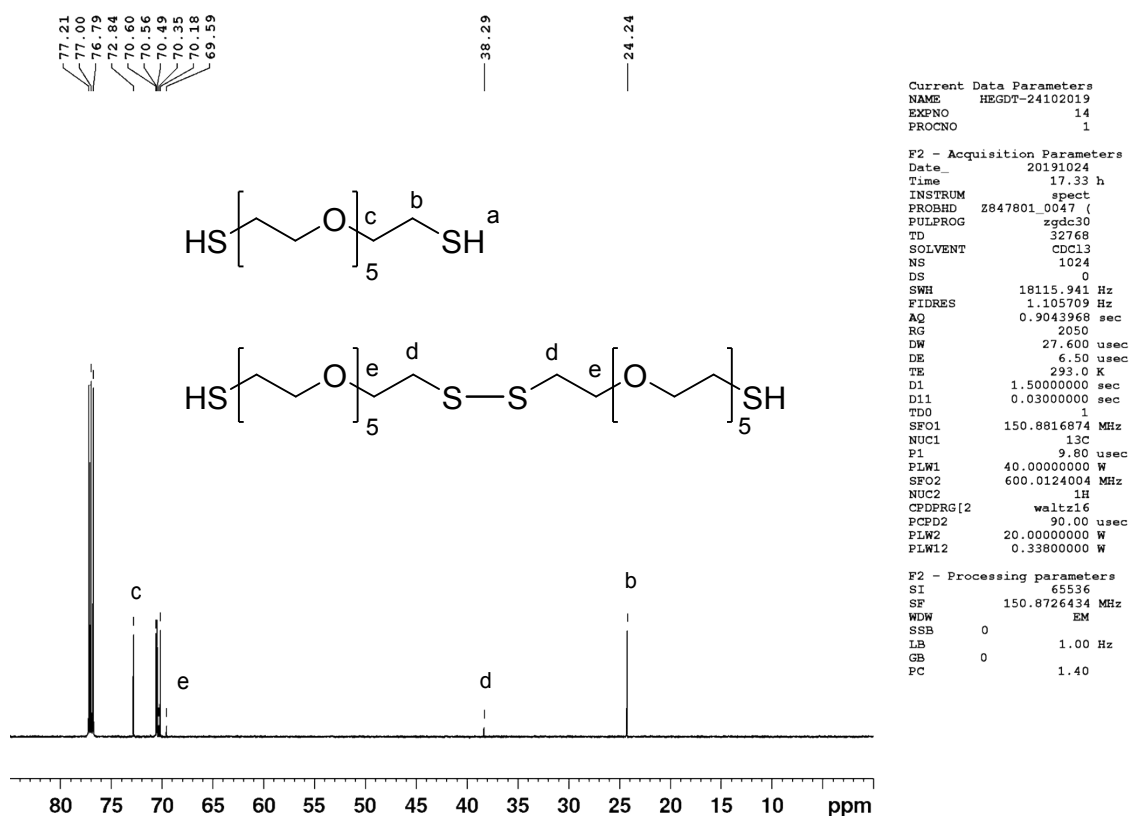


Fig. SII. 3. ^{13}C NMR spectrum of hexa(ethylene glycol)dithiol (HEGDT) in CDCl_3 .

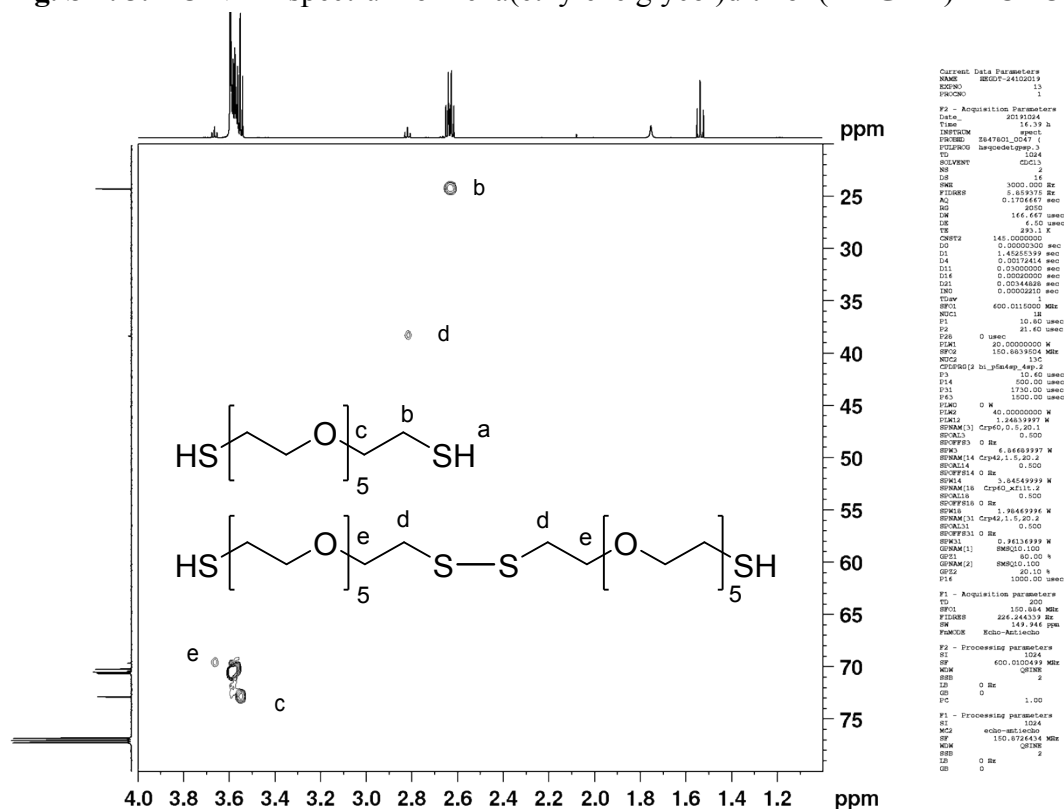


Fig. SII. 4. ^1H - ^{13}C HSQC NMR spectrum of hexa(ethylene glycol)dithiol (HEGDT) in CDCl_3 .

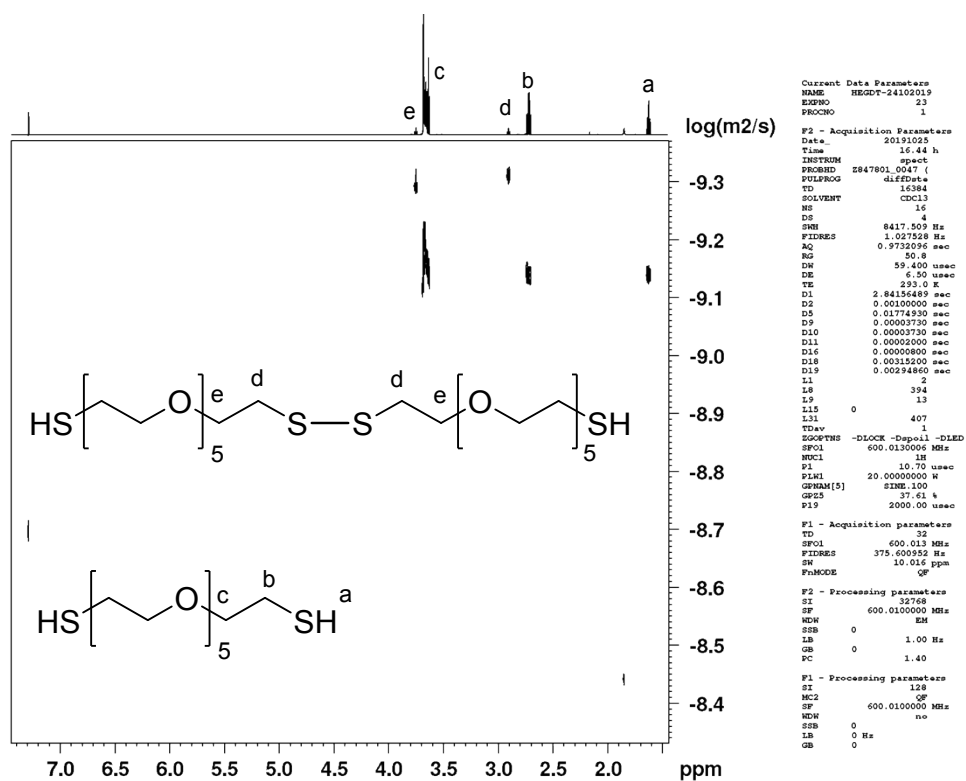


Fig. SII. 5. DOSY NMR spectrum of hexa(ethylene glycol)dithiol (HEGDT) in CDCl₃.

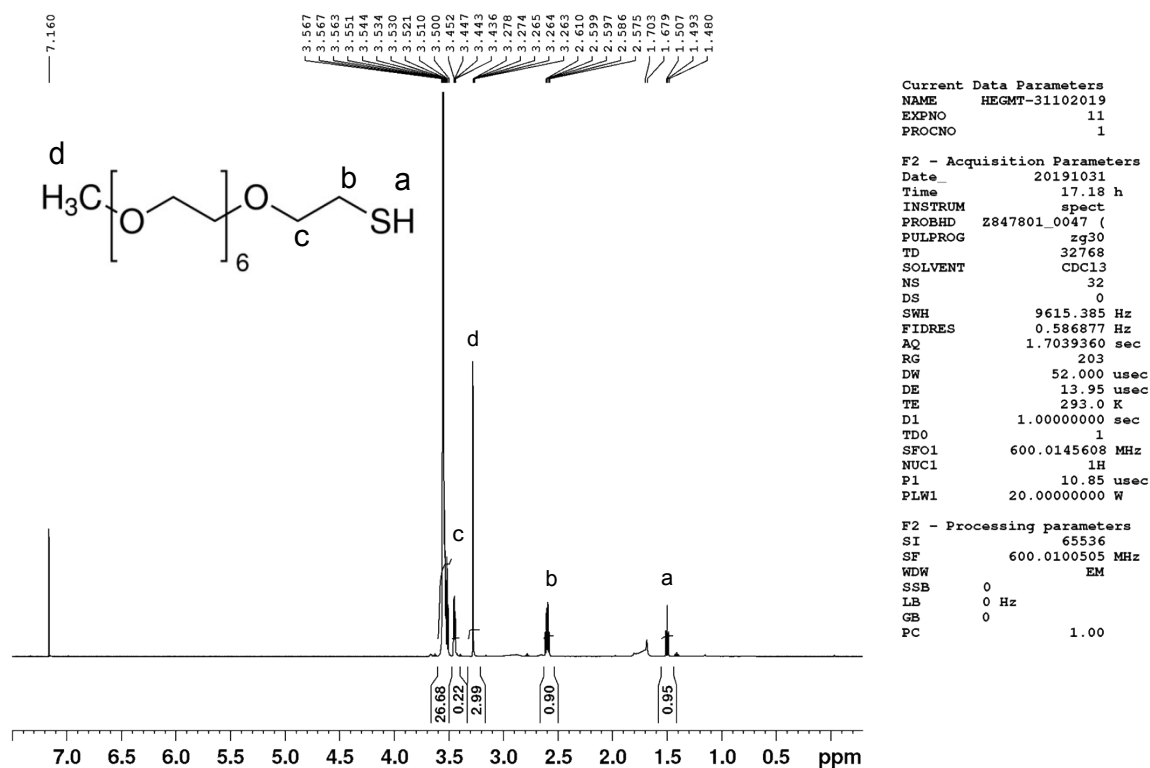


Fig. SII. 6. ¹H NMR spectrum of O-(2-Mercaptoethyl)-O'-methyl-hexa(ethylene glycol) (HEGMT) in CDCl₃.

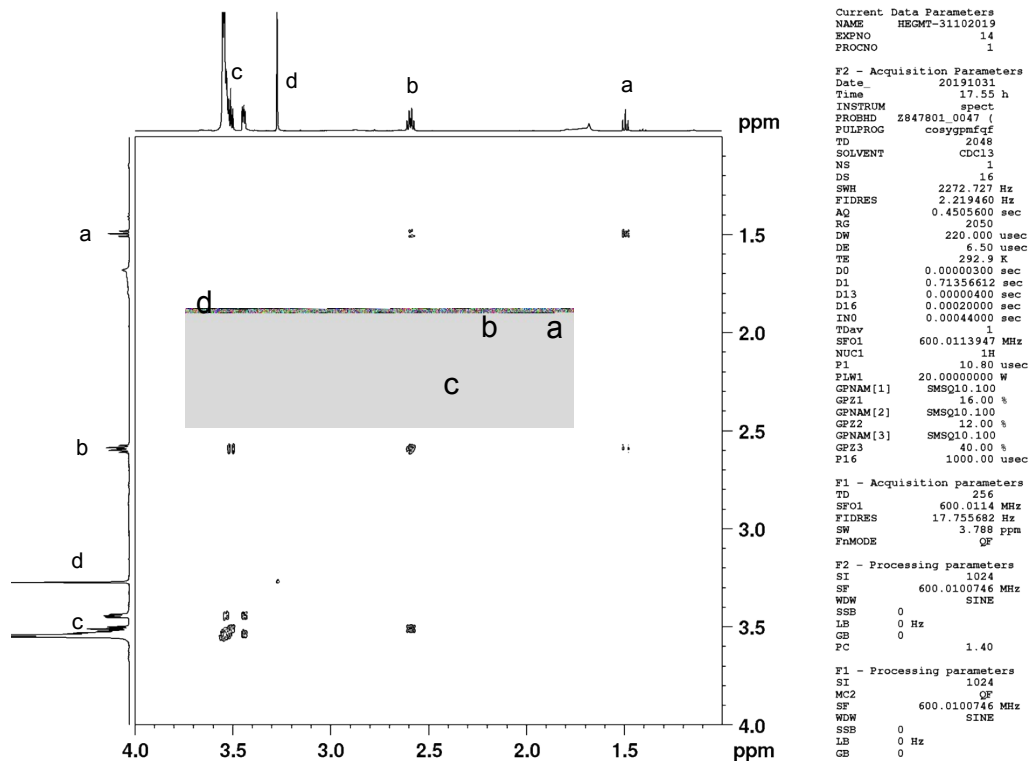


Fig. SII 7. ^1H - ^1H COSY NMR spectrum of O-(2-Mercaptoethyl)-O'-methyl-hexa(ethylene glycol) (HEGMT) in CDCl_3 .

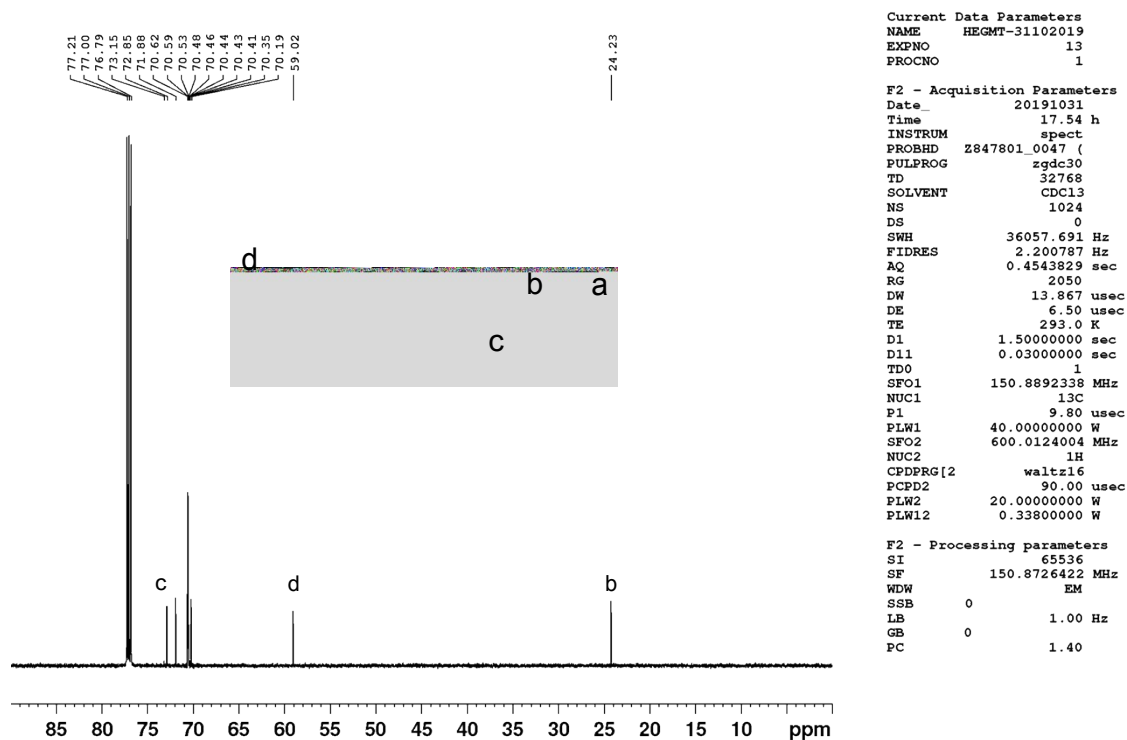
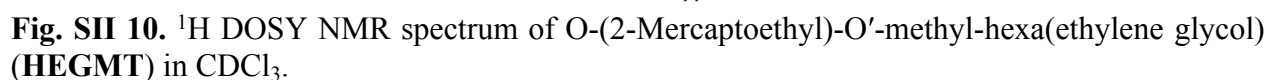
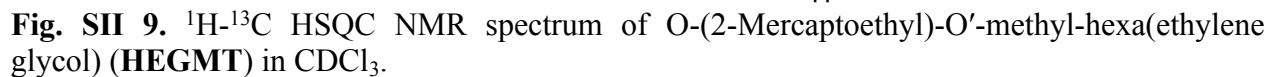


Fig. SII 8 ^{13}C NMR spectrum of O-(2-Mercaptoethyl)-O'-methyl-hexa(ethylene glycol) (HEGMT) in CDCl_3 .



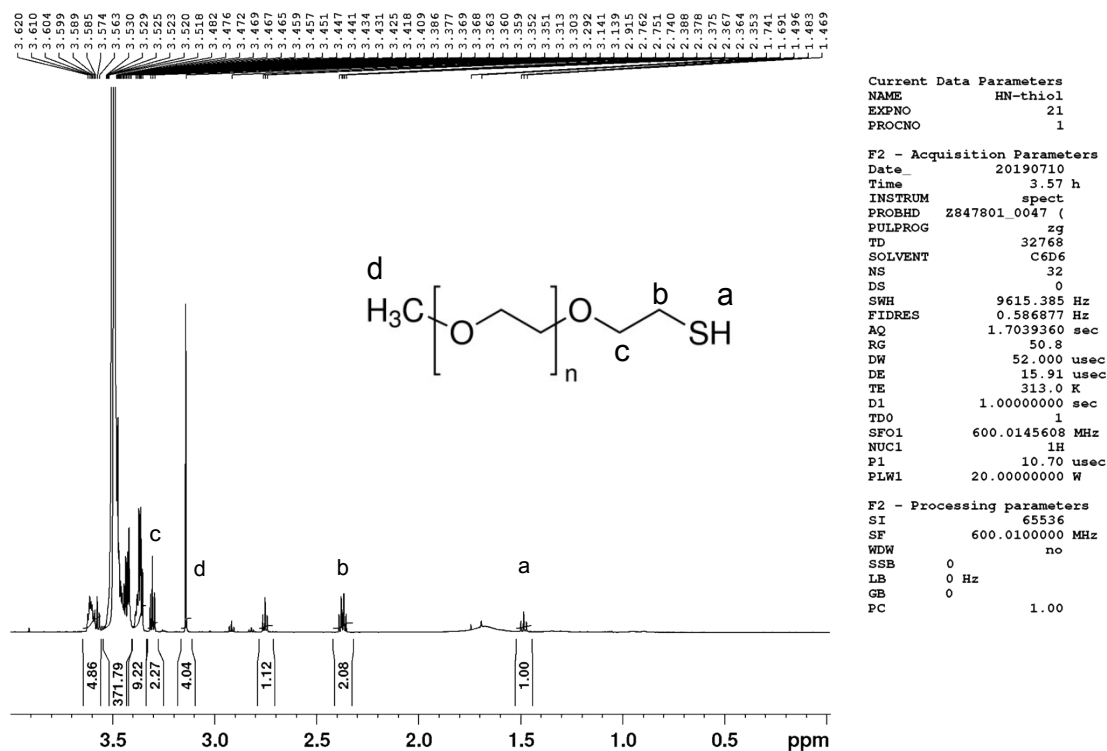


Fig. SII 11. ^1H NMR spectrum of poly(ethylene glycol)methyl ether thiol (PEGMET) taken in C_6D_6 ($n=45$).

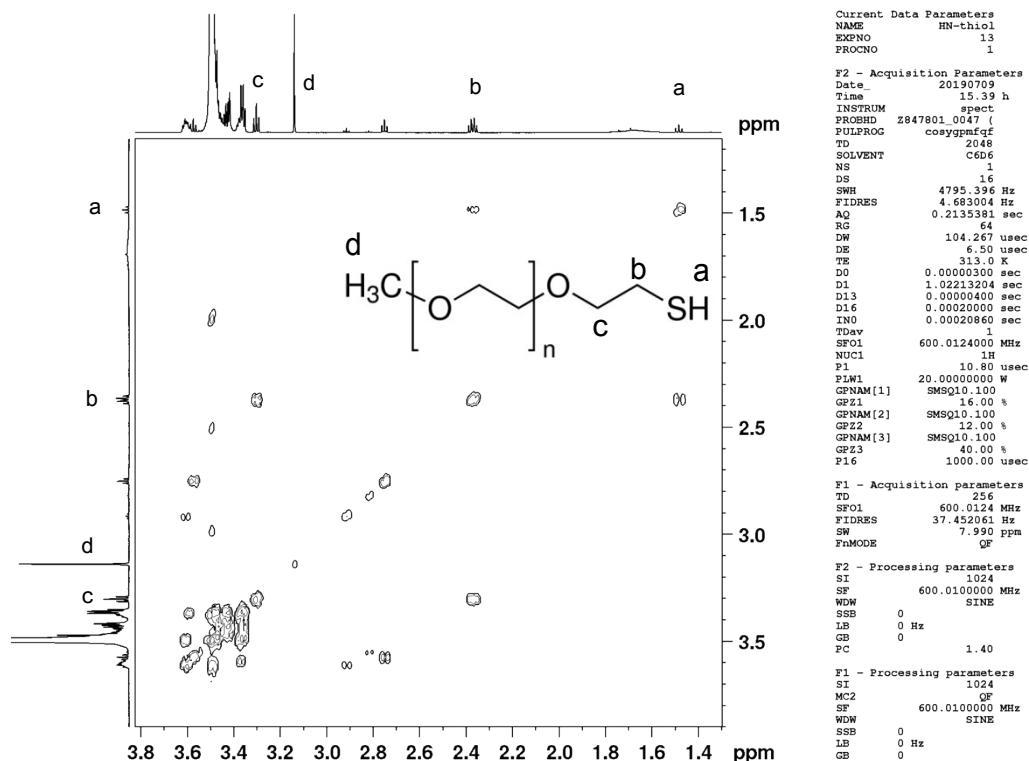


Fig. SII 12. ^1H - ^1H COSY NMR spectrum of poly(ethylene glycol)methyl ether thiol (PEGMET) taken in C_6D_6 ($n=45$).

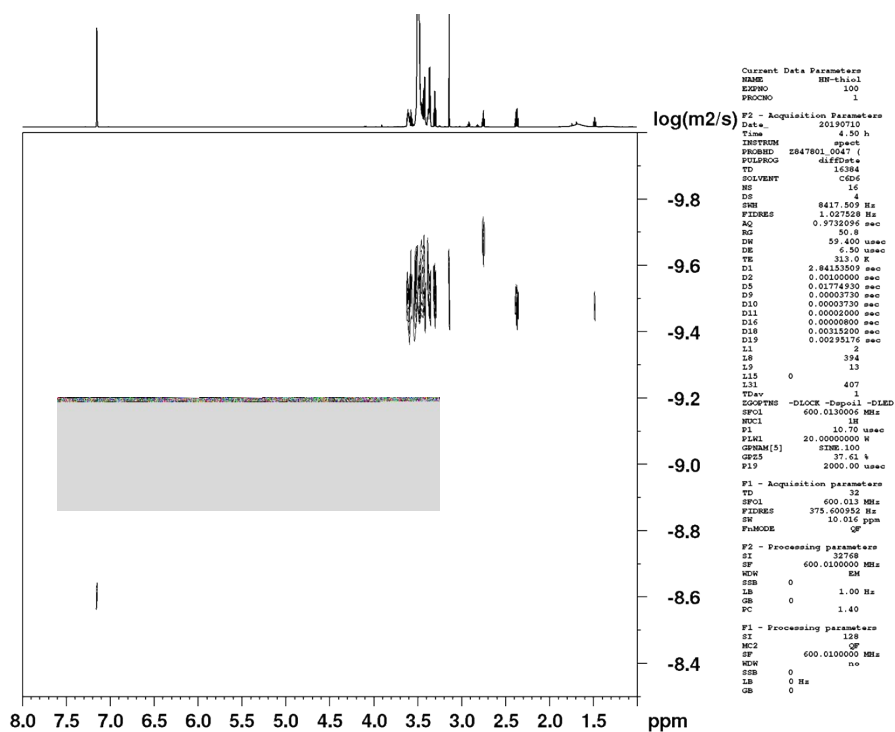


Fig. S II 15. ^1H DOSY NMR spectrum of poly(ethylene glycol)methyl ether thiol (PEGMET) taken in C_6D_6 ($n=45$).

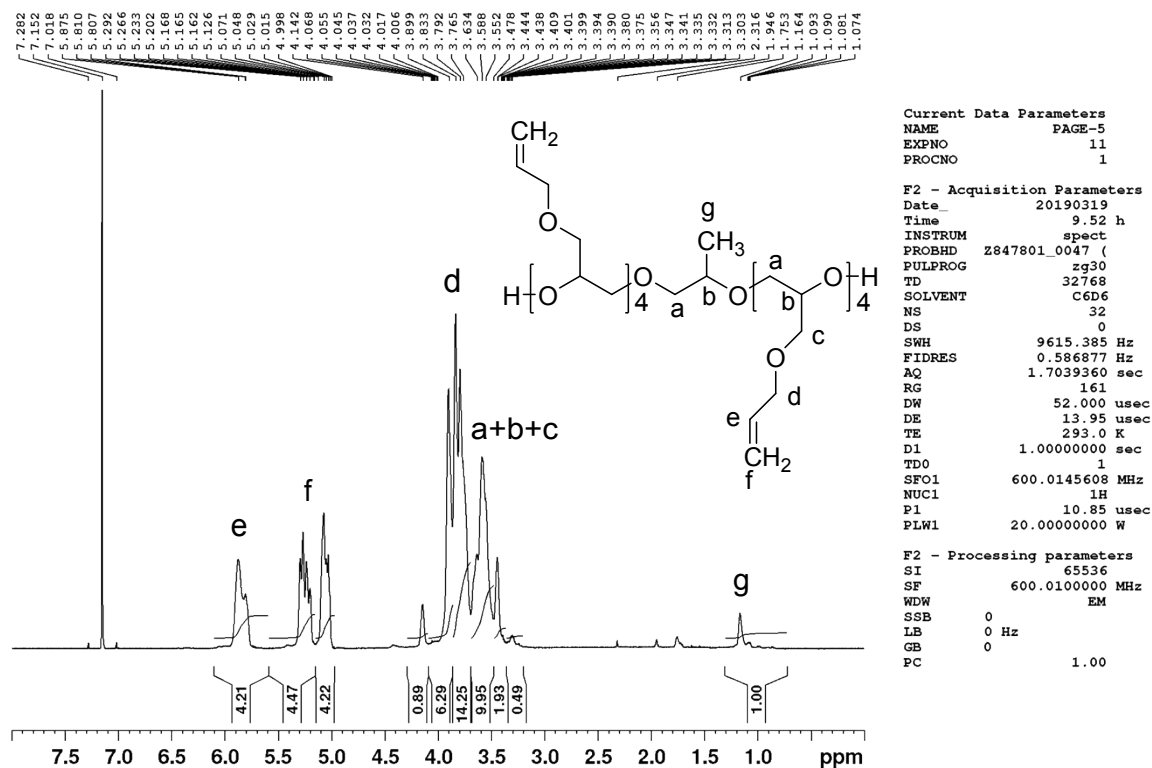


Fig. SII 16. ^1H NMR spectrum of poly(allyl glycidyl ether) PAGE precursor in C_6D_6 .

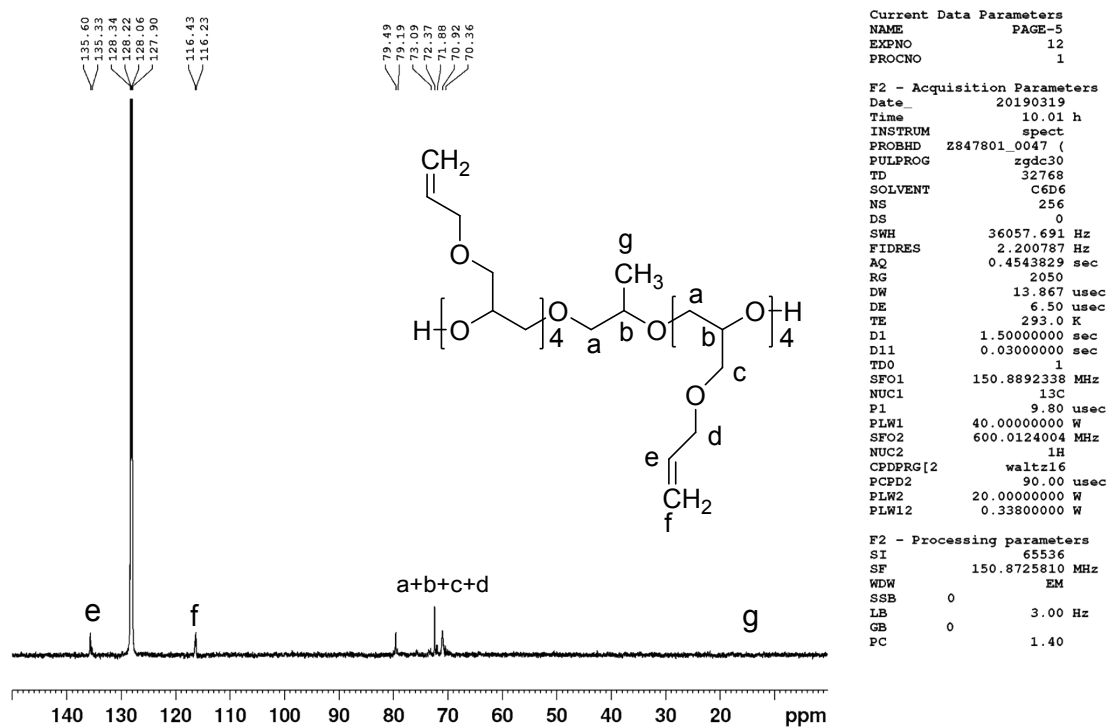


Fig. SII 17. ^{13}C NMR spectrum of poly(allyl glycidyl ether) **PAGE** precursor in C_6D_6 .

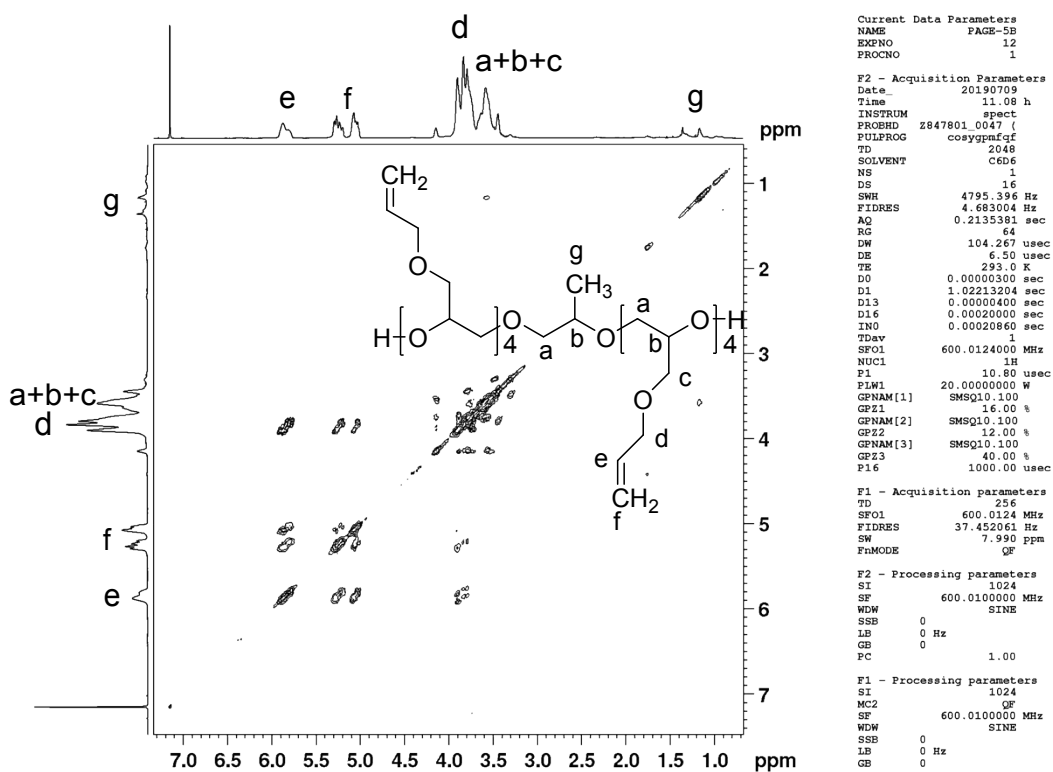
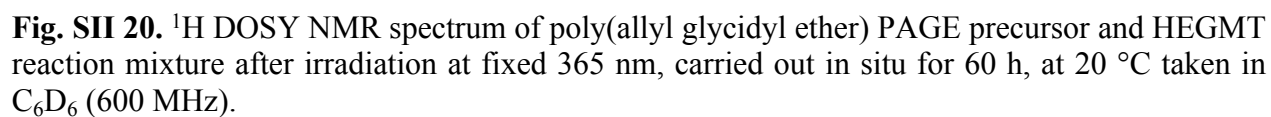
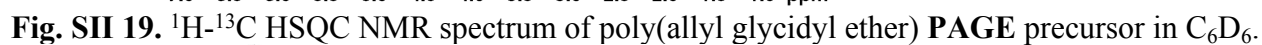


Fig. SII 18. ^1H - ^1H COSY NMR spectrum of poly(allyl glycidyl ether) **PAGE** precursor in C_6D_6 .



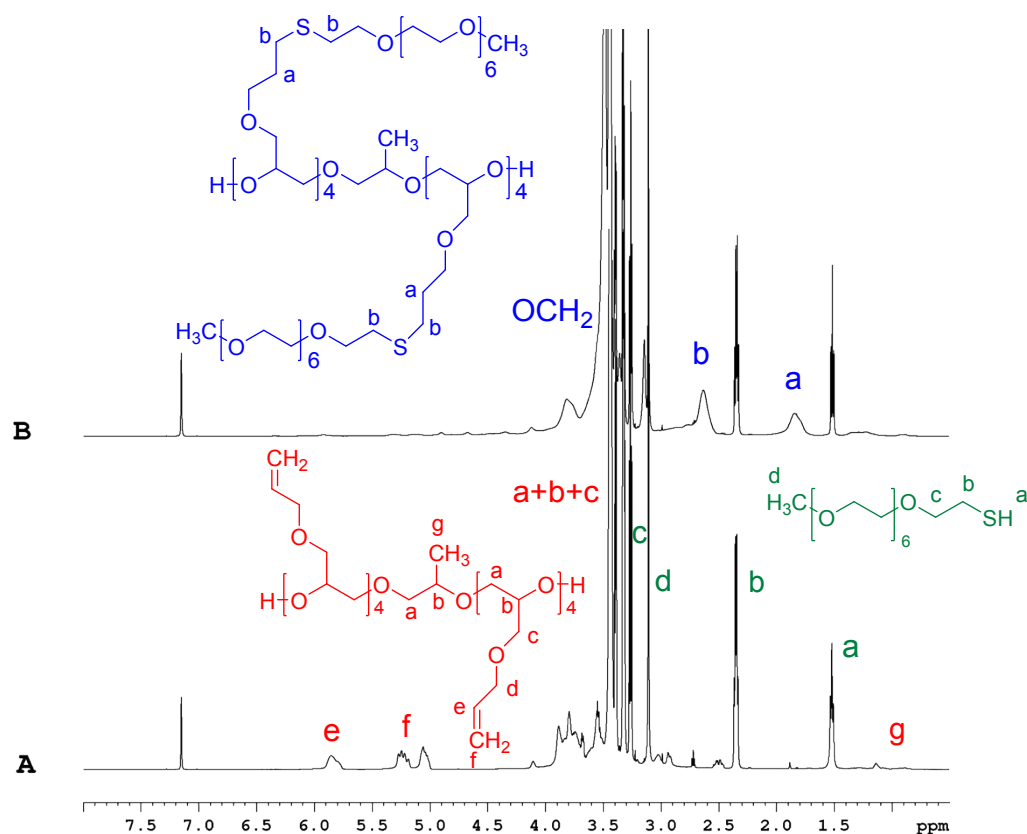


Fig. SII 21. ^1H NMR spectrum of PAGE precursor and HEGMT reaction mixture before (A) and after (B) irradiation at fixed 365 nm, carried out in situ for 60 h, at 20 °C taken in C_6D_6 .

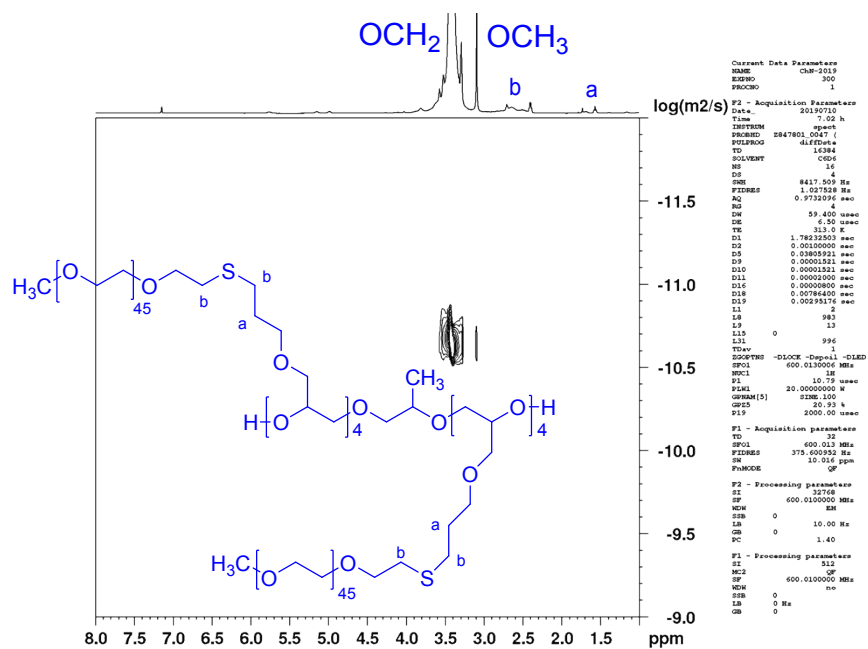


Fig. SII.22. ^1H DOSY NMR spectrum of mixture of PAGE precursor and PEGMET after irradiation at fixed 365 nm, carried out “in situ” for 114 h, at 40 °C taken in C_6D_6 .

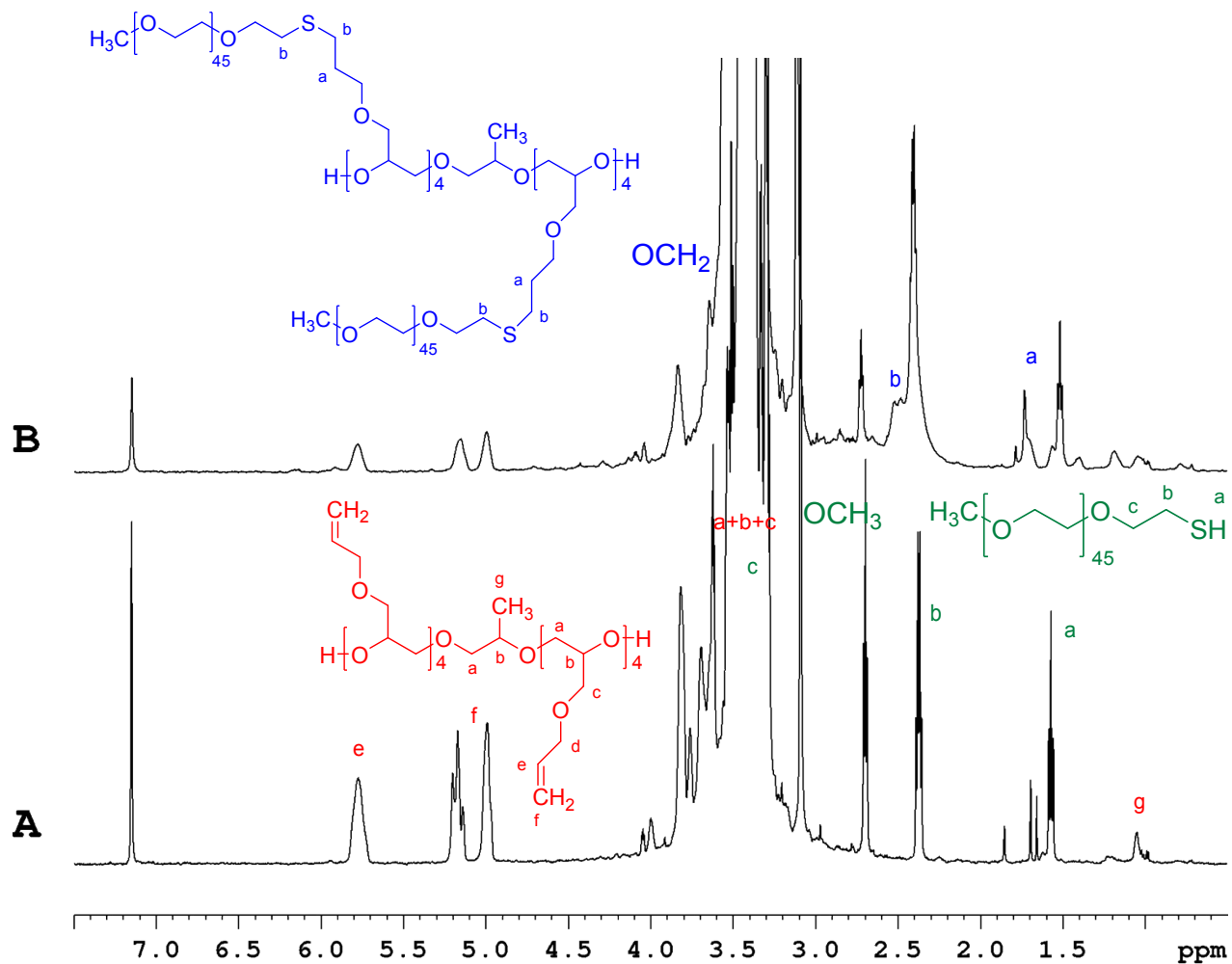


Fig. SII 23. ^1H NMR spectrum of mixture of PAGE precursor and PEGMET before (A) and after (B) irradiation after irradiation at fixed 365 nm, carried out “in situ” for 114 h, at 40 °C taken in C_6D_6 .

III. GPC elugrams.

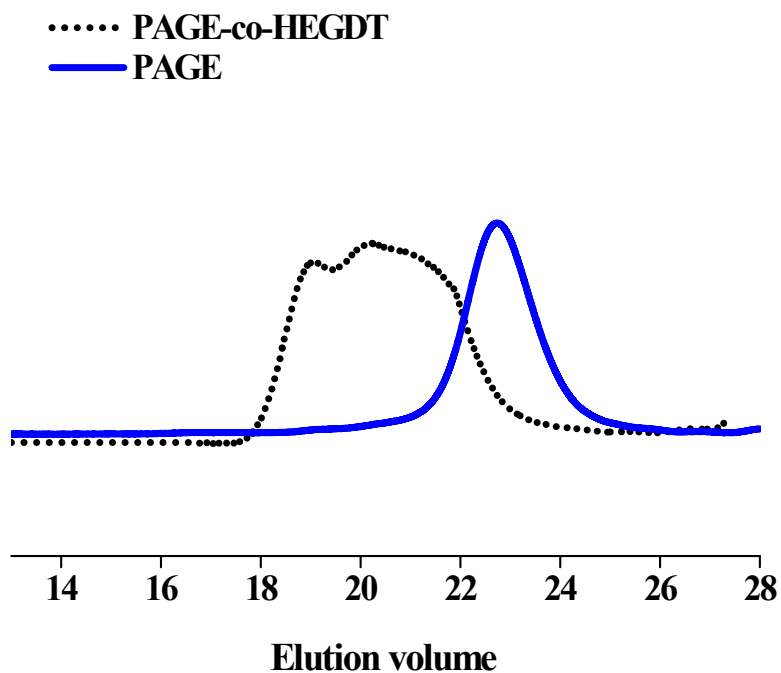


Fig. SIII 1. GPC traces of PAGE (blue) and PAGE-HEGDT (black) soluble fraction in THF as eluent (RI trace, THF).

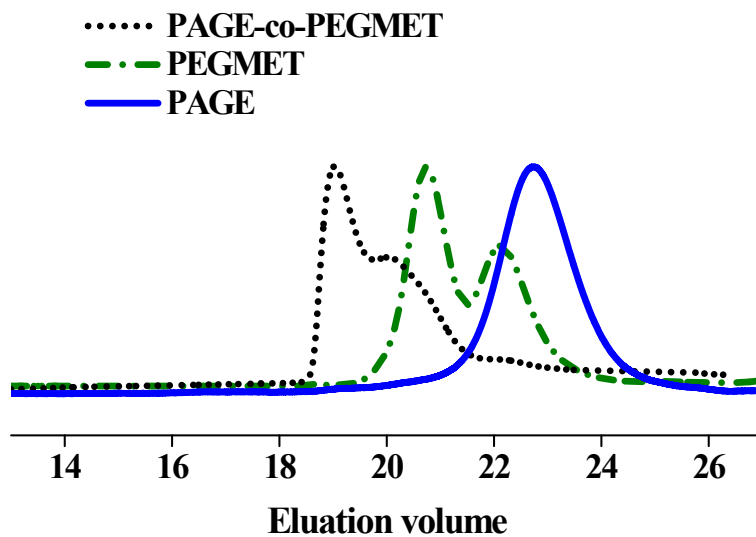


Fig. SIII 2. GPC traces of (PAGE (blue), PEGMET (green) and PAGE-PEGMET copolymer (black) (RI trace, THF).

IV. “In situ” irradiation NMR spectroscopy.



Fig. S IV 1. LED source and optical fiber to the NMR test tube used for “in situ” UV-irradiation NMR spectroscopy.

“In situ” irradiation NMR spectroscopy includes “in situ” photoinitiation enabled by LEDs in combination with the all variety of NMR methods. The self-made LED set-up includes control unit (right top) with choice of three LED sources coupled to optical fiber (left), which end is inserted into a coaxial NMR insert (bottom right). The usage of coaxial insert provides uniform illumination of the whole reaction solution thus ensuring irradiated volume matches the one detected by NMR coil.