- Supporting Information –

Poly(ethylene glycol) with Multiple Aldehyde Functionalities Opens up a Rich and Versatile Post-Polymerization Chemistry

*Jan Blankenburg[‡§], Kamil Maciol[‡], Christoph Hahn[‡], Holger Frey[‡]**

‡ Institute of Organic Chemistry, Johannes Gutenberg University Mainz, Duesbergweg 10-14, 55128 Mainz, Germany

§ Graduate School Materials Science in Mainz, Staudinger Weg 9, 55128 Mainz, Germany

*(H.F.) E-Mail: hfrey@uni-mainz.de

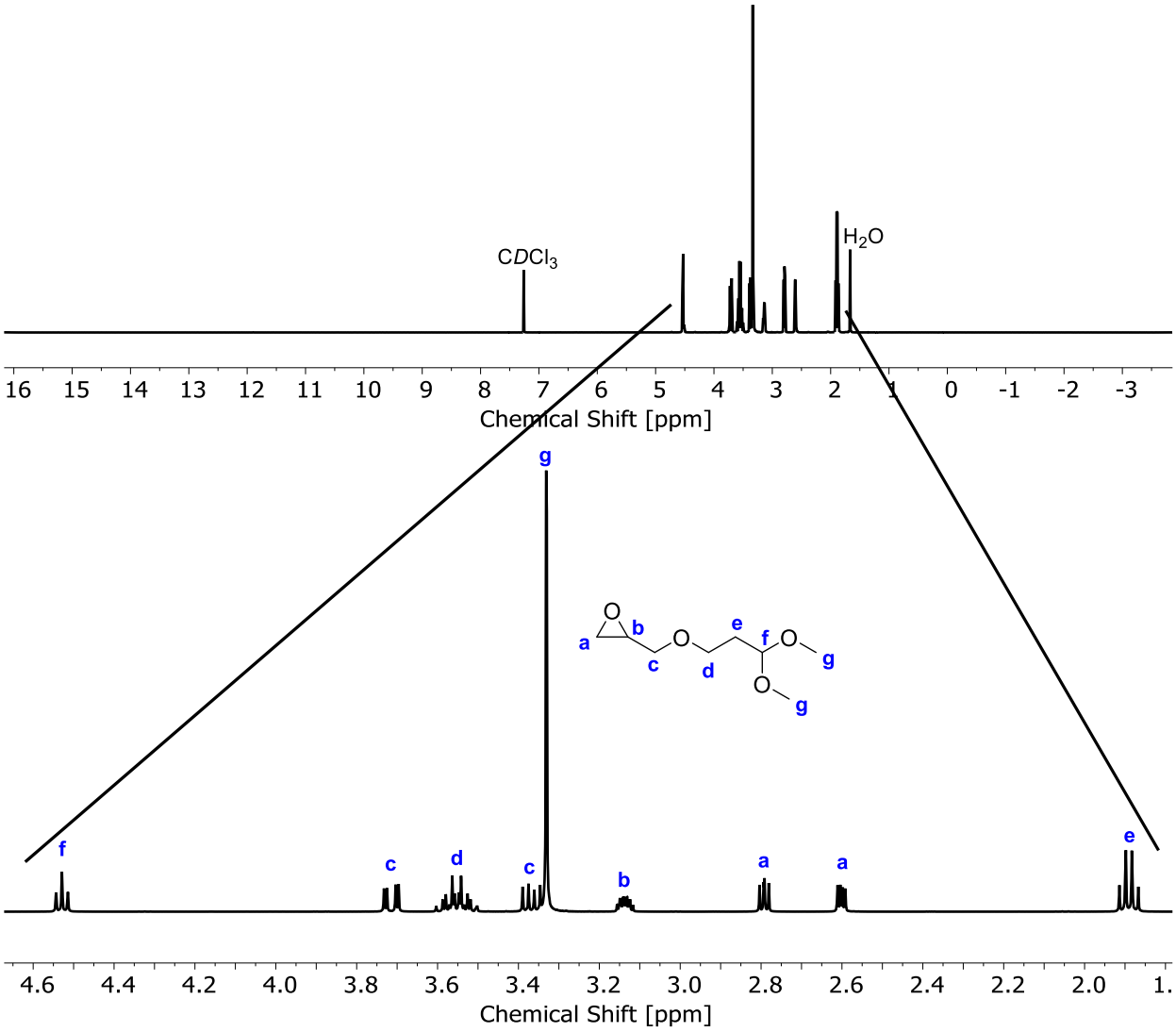

Figure S1. ^{1}H NMR spectrum (400 MHz, C*D*Cl$_3$) of DMPGE.

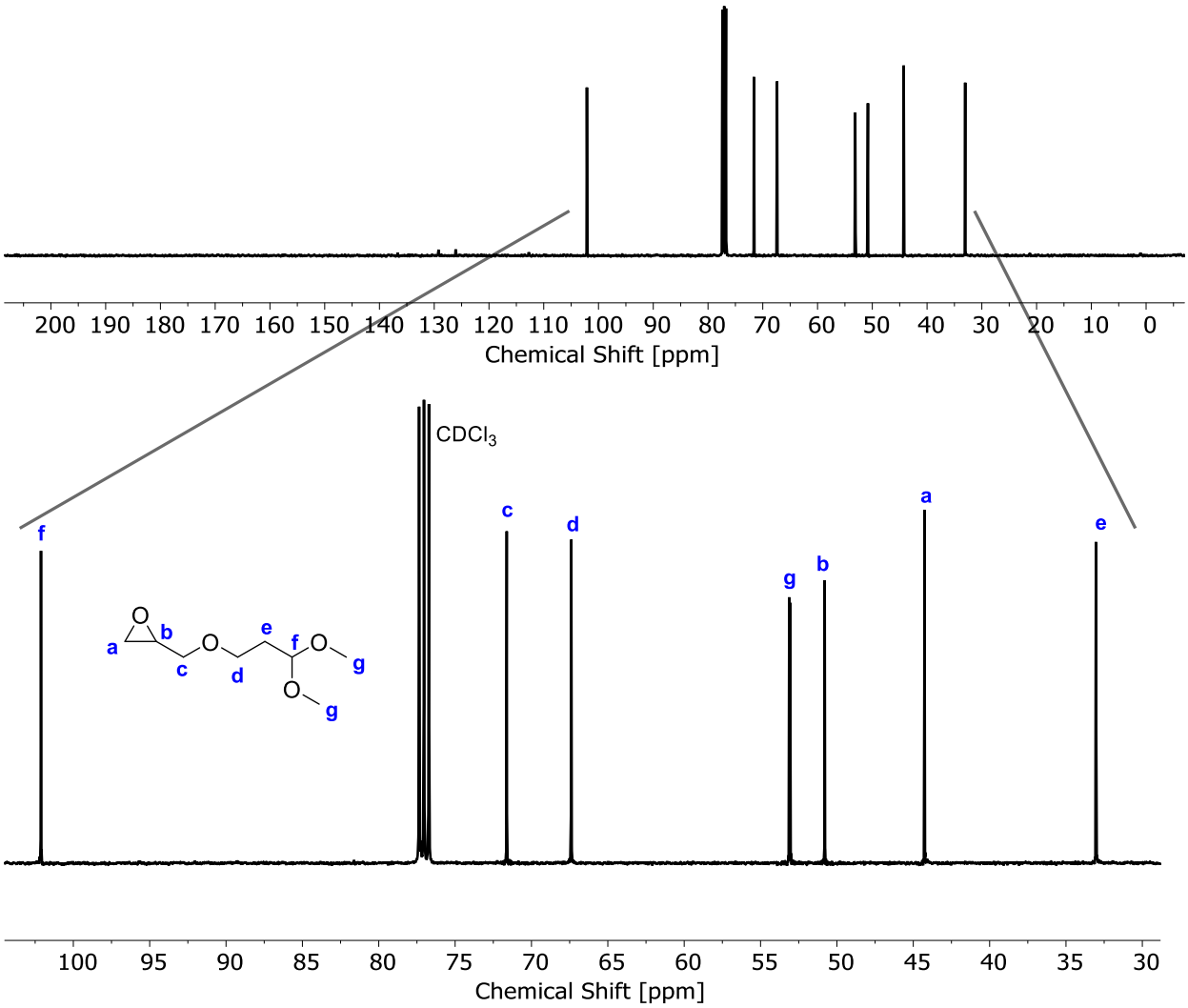

Figure S2. ^{13}C NMR spectrum (100 MHz, C*D*Cl$_3$) of DMPGE.

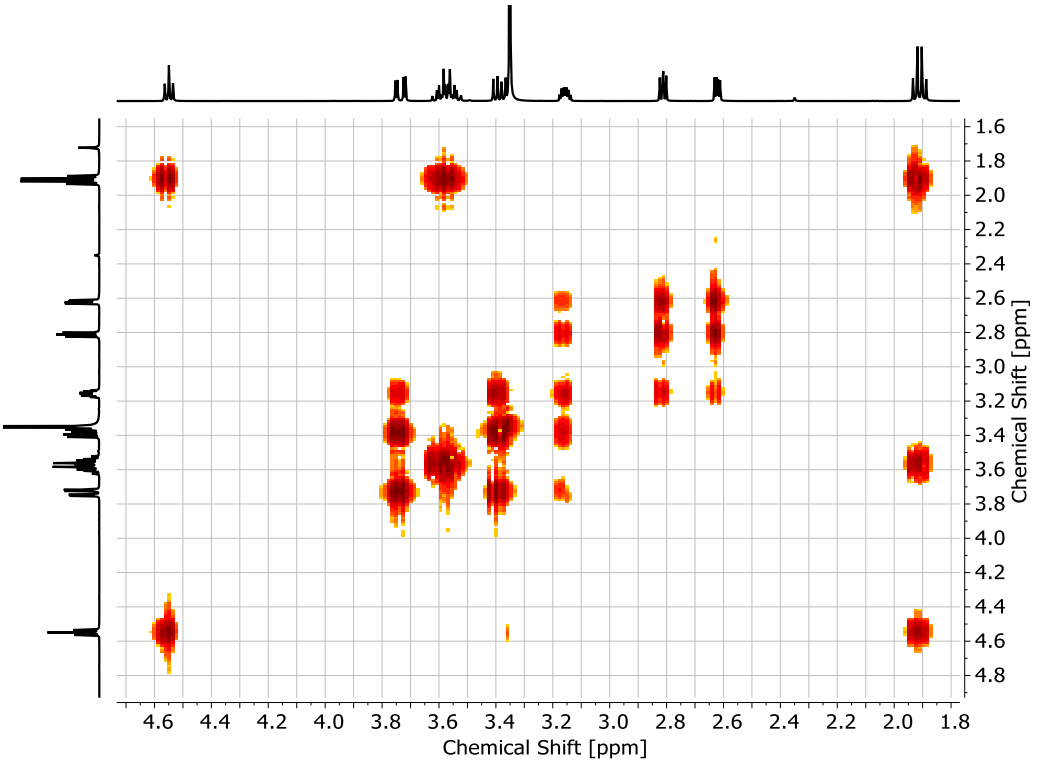

Figure S3. ^{1}H, ^{1}H COSY NMR spectrum (400 MHz, C*D*Cl$_3$) of DMPGE.

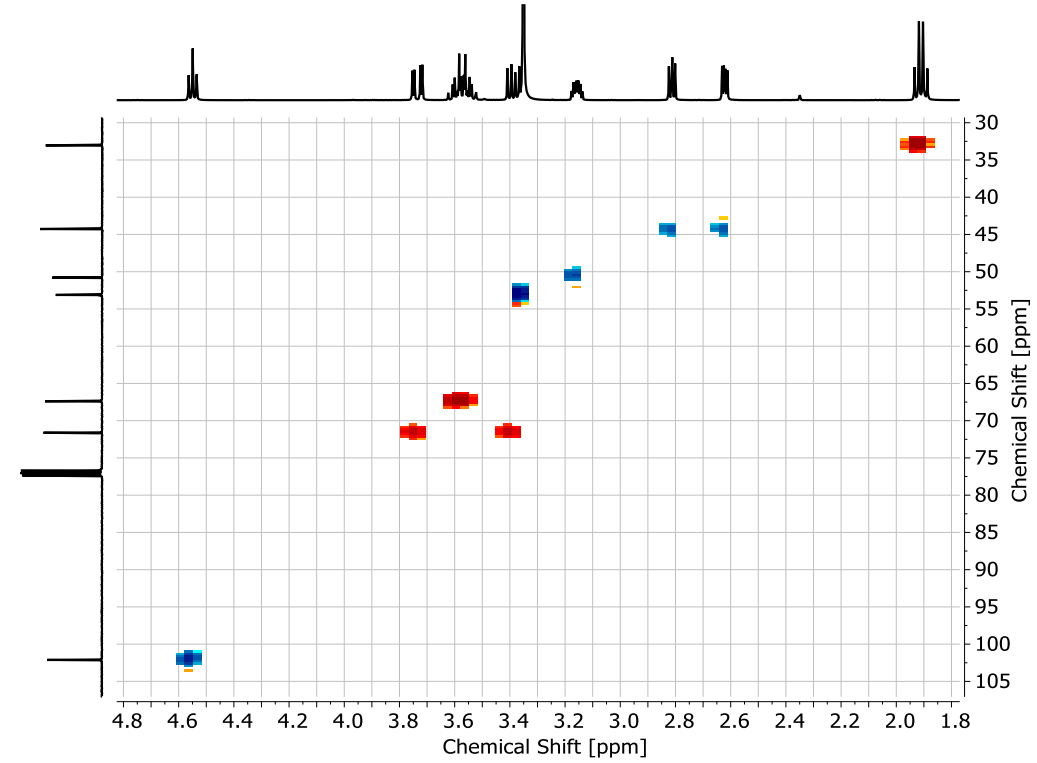

Figure S4. ^{1}H, ^{13}C HSQC NMR spectrum (C*D*Cl$_3$) of DMPGE.

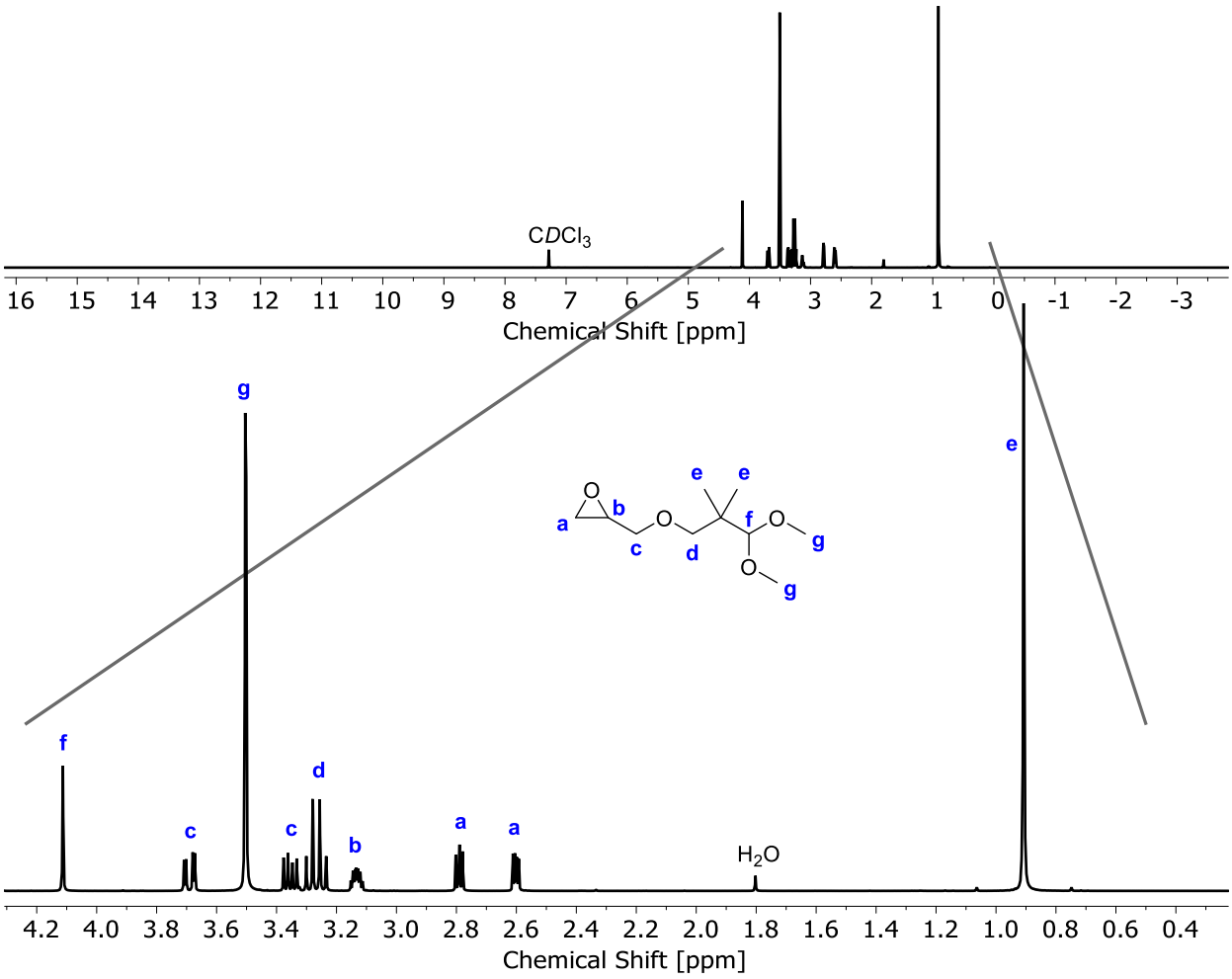

Figure S5. ^{1}H NMR spectrum (400 MHz, C*D*Cl$_3$) of DDPGE.

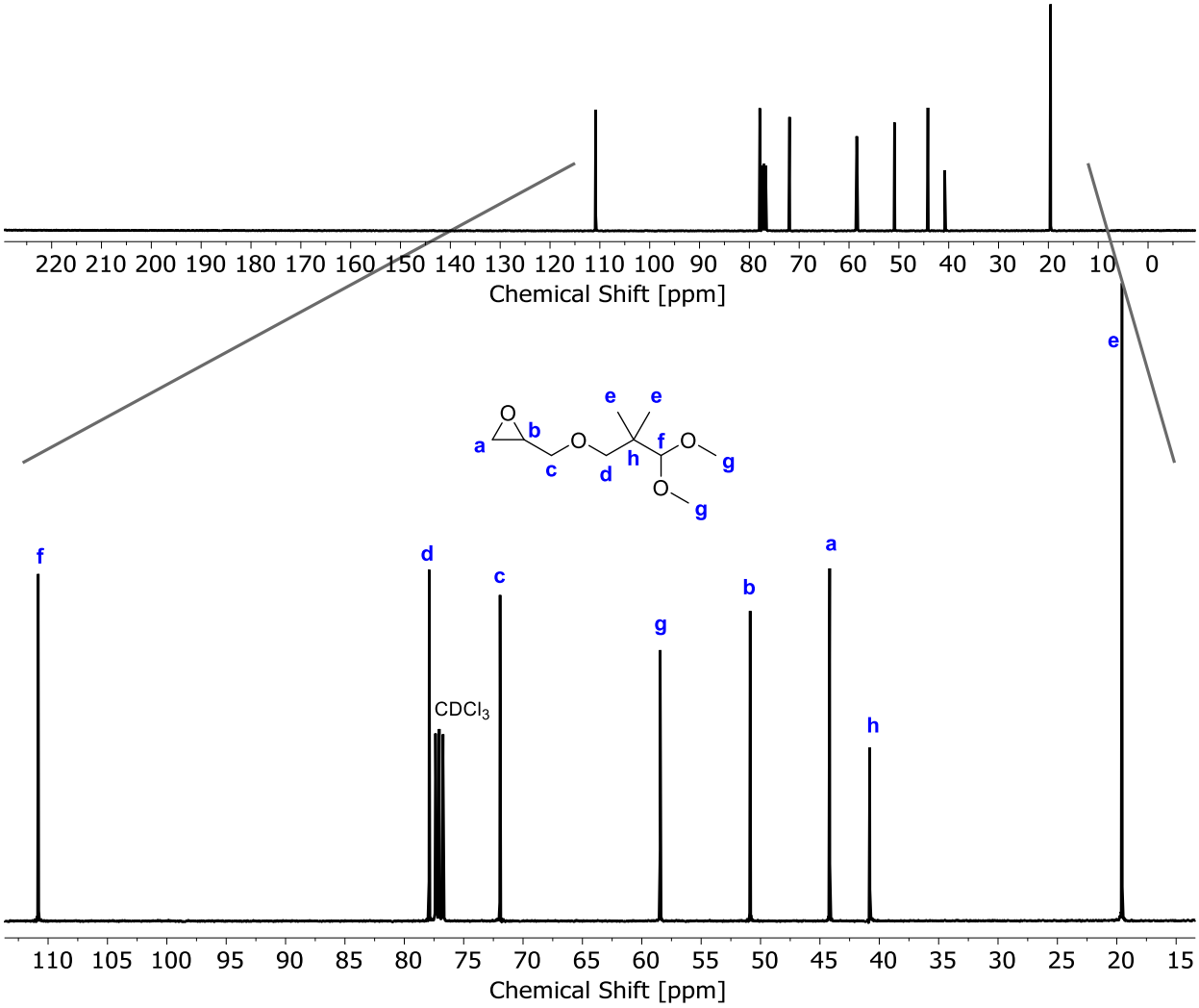

Figure S6. ^{13}C NMR spectrum (100 MHz, C*D*Cl$_3$) of DDPGE.

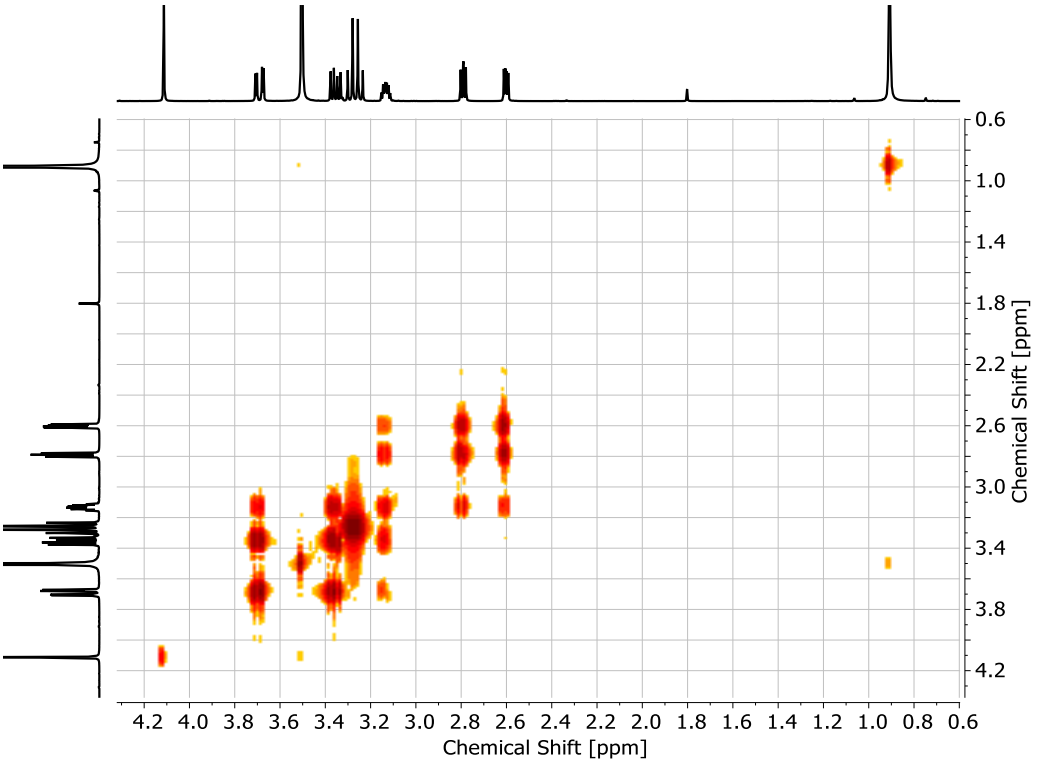

Figure S7. ^{1}H, ^{1}H COSY NMR spectrum (400 MHz, C*D*Cl$_3$) of DDPGE.

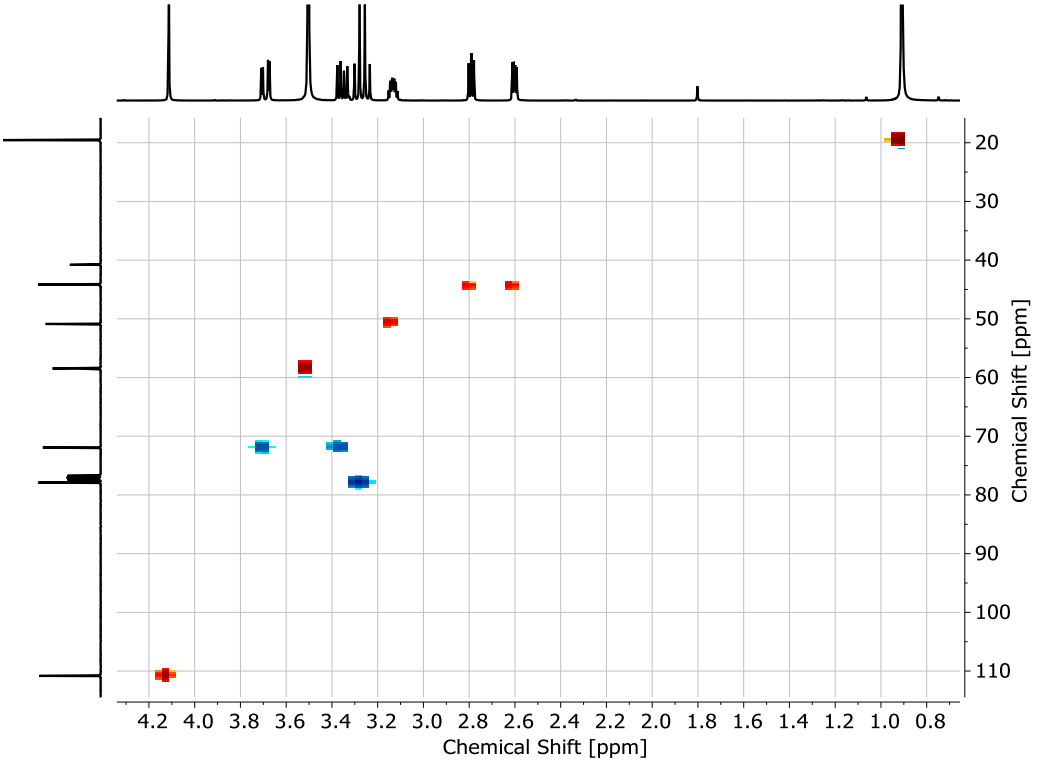

Figure S8. ^{1}H, ^{13}C HSQC NMR spectrum (C*D*Cl$_3$) of DDPGE.

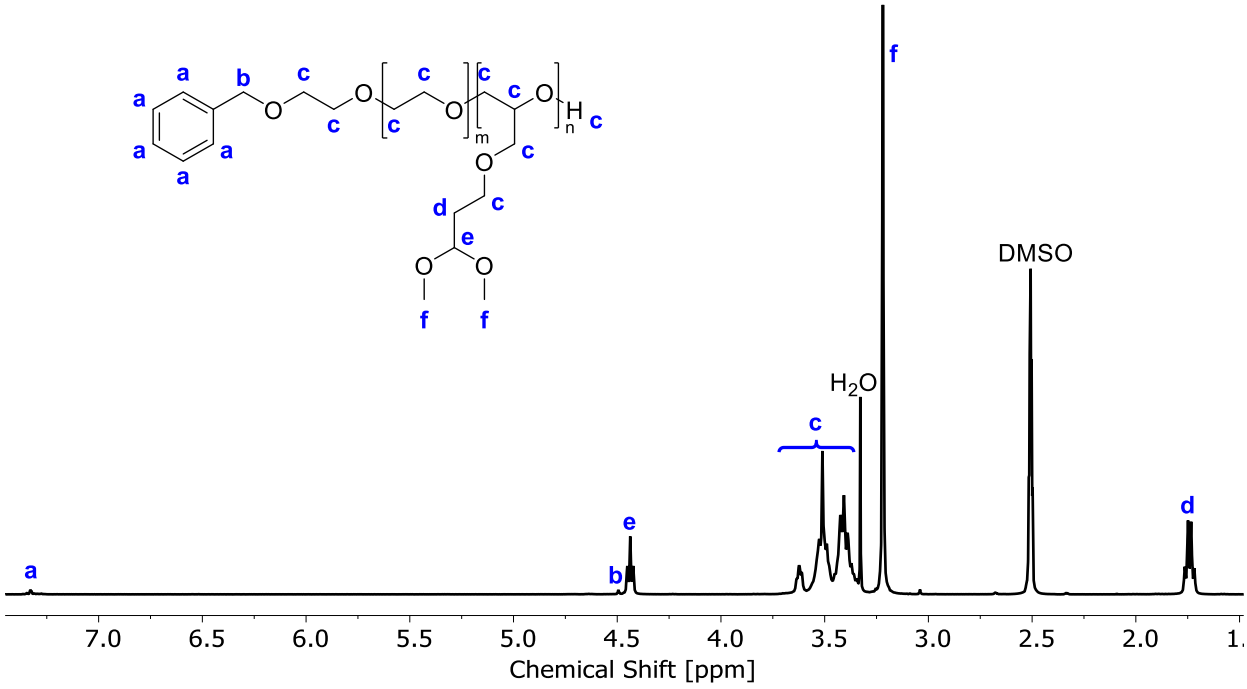

Figure S9. ^{1}H NMR spectrum (400 MHz, DMSO-d_6) of P(EO$_{42}$-*co*-DMPGE$_{56}$).

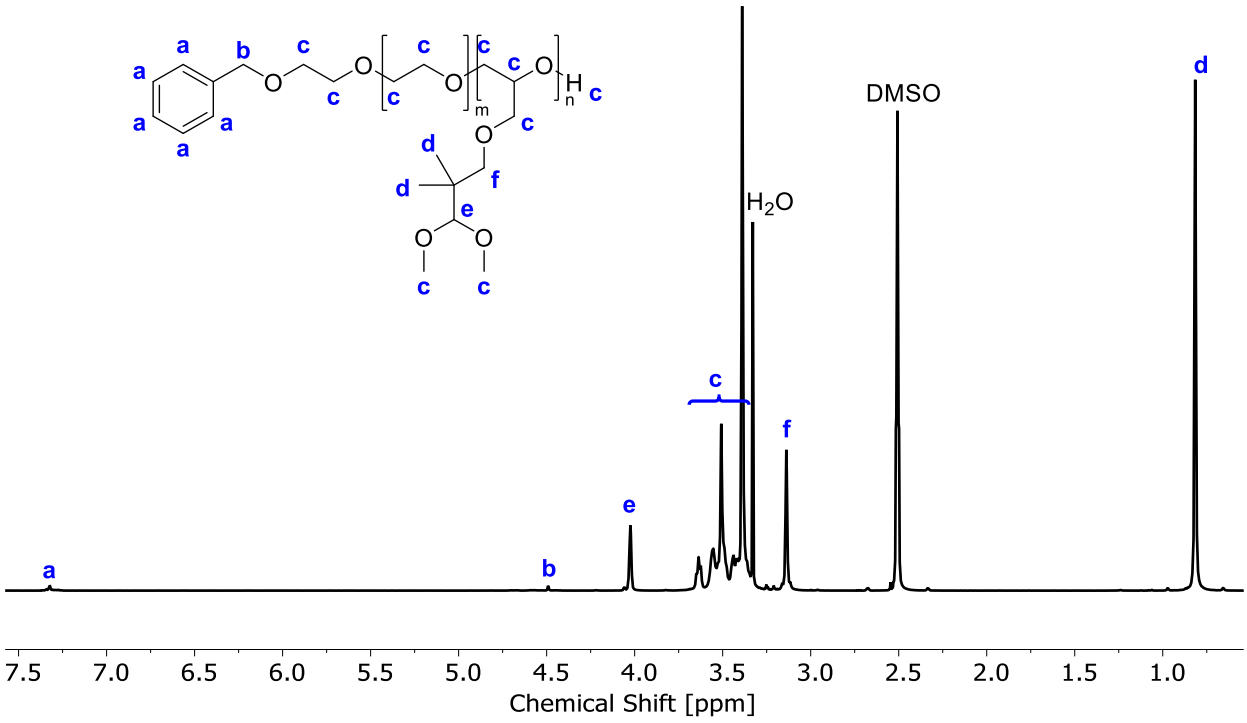

Figure S10. ^{1}H NMR spectrum (400 MHz, DMSO-d_6) of P(EO$_{39}$-*co*-DDPGE$_{43}$).

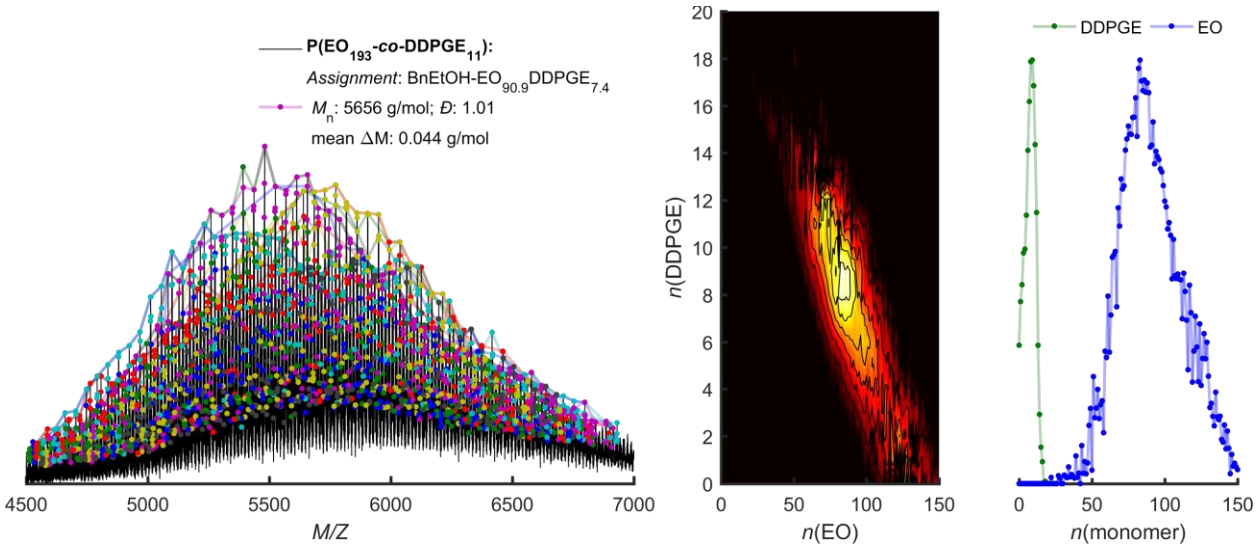

Figure S11. MALDI TOF spectra of P(EO$_{193}$-*co*-DDPGE$_{11}$) copolymers with peak assignment and extracted copolymer composition distribution. A detailed explanation of the evaluation procedure leading to the different signal series can be found elsewhere.[1]

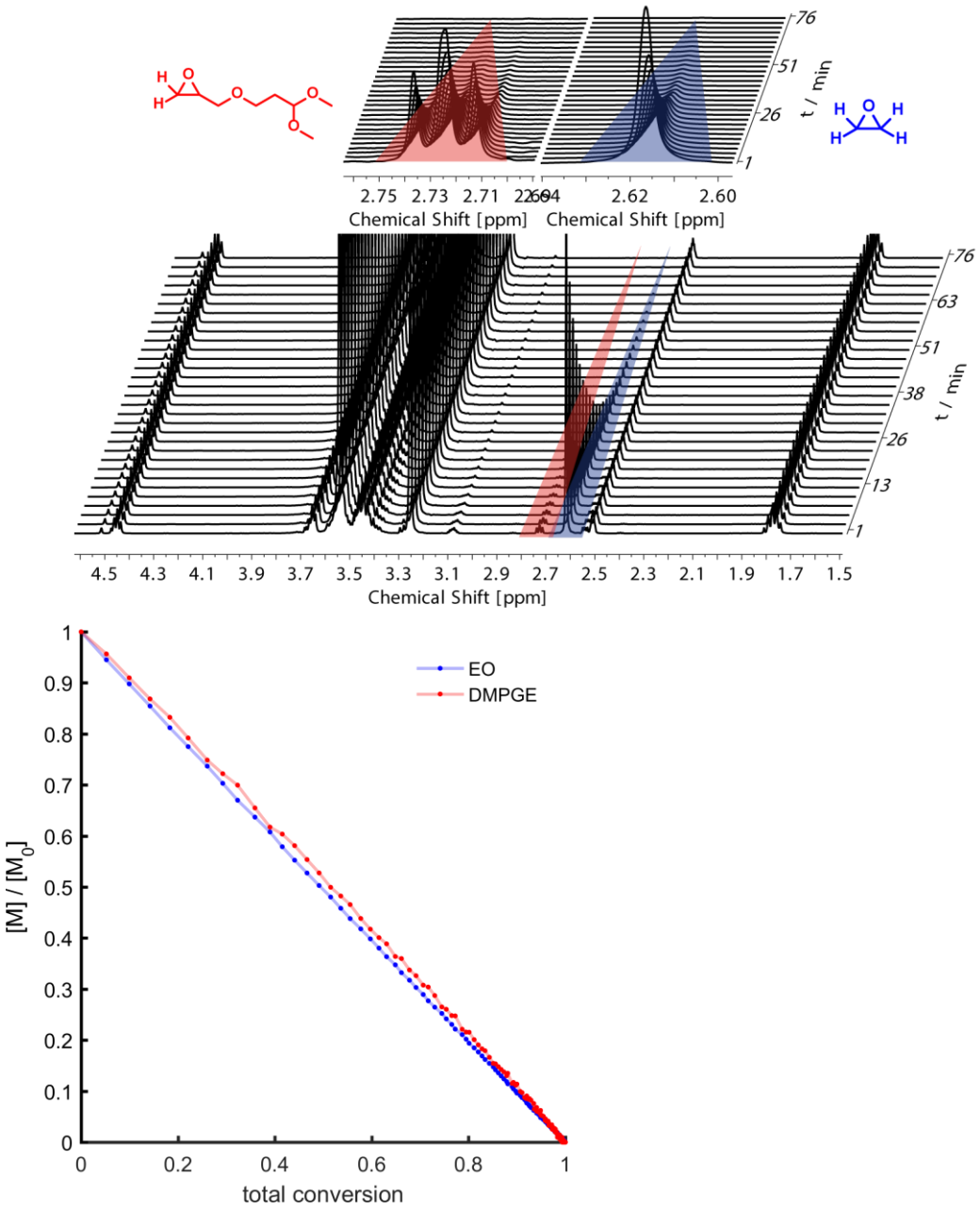

Figure S12. Evaluated signals in ^{1}H NMR copolymerization kinetics experiment of EO and DMPGE (top); normalized concentration as a function of total conversion (bottom).

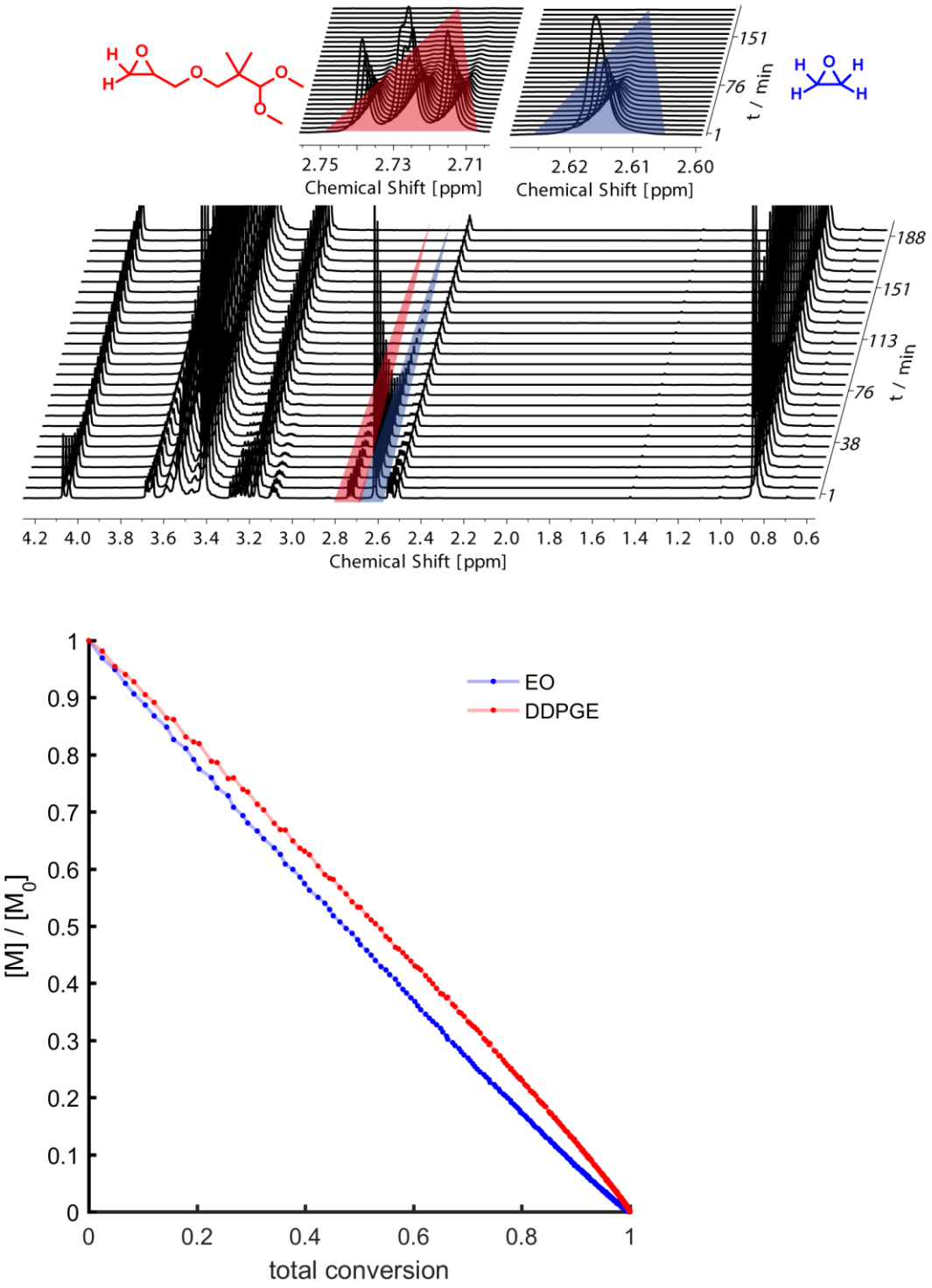

Figure S13. Evaluated signals in ^{1}H NMR copolymerization kinetics experiment of EO and DDPGE (top); normalized concentration as a function of total conversion (bottom).

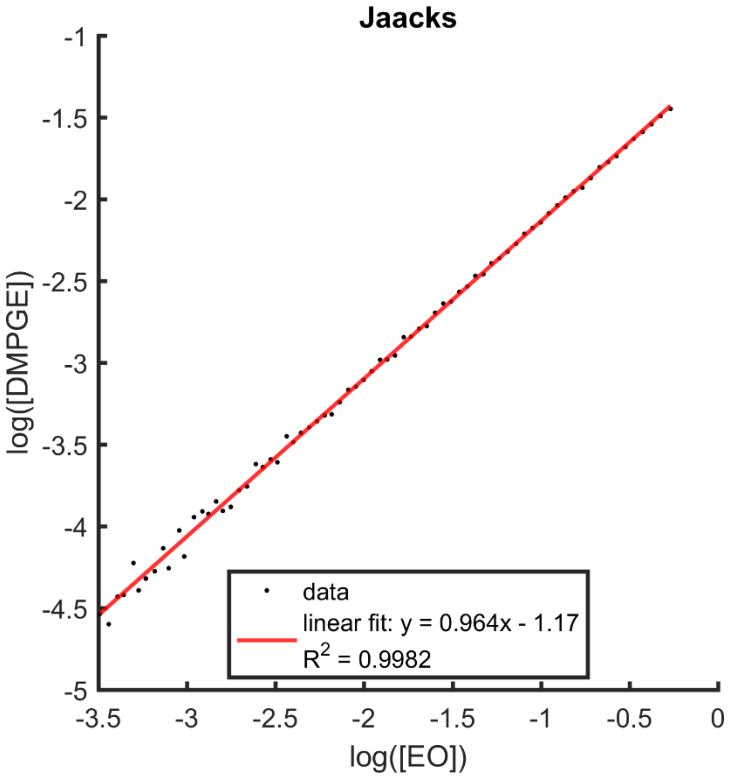

Figure S14. Jaacks-fit of copolymerization of EO and DMPGE.

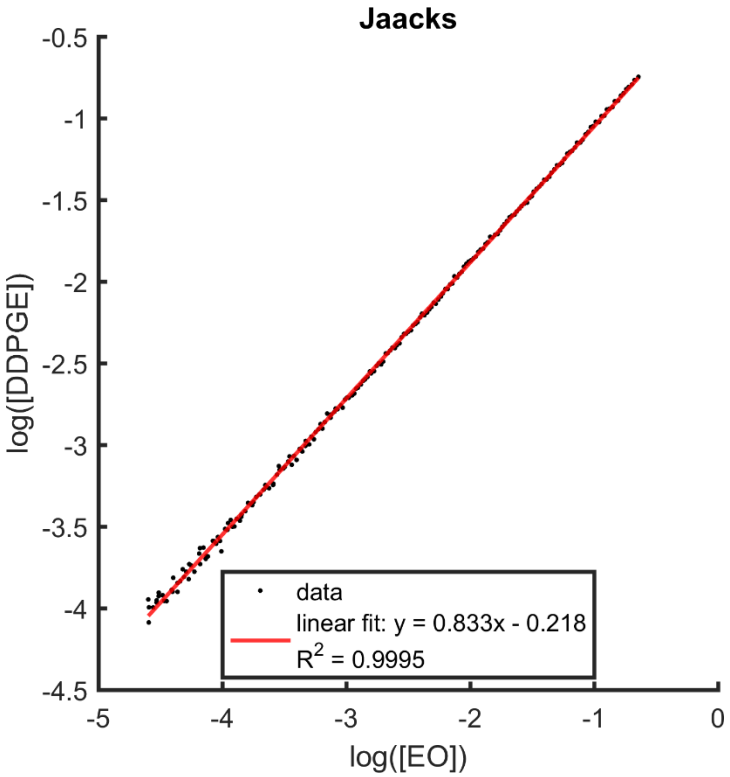

Figure S15. Jaacks-fit of copolymerization of EO and DDPGE.

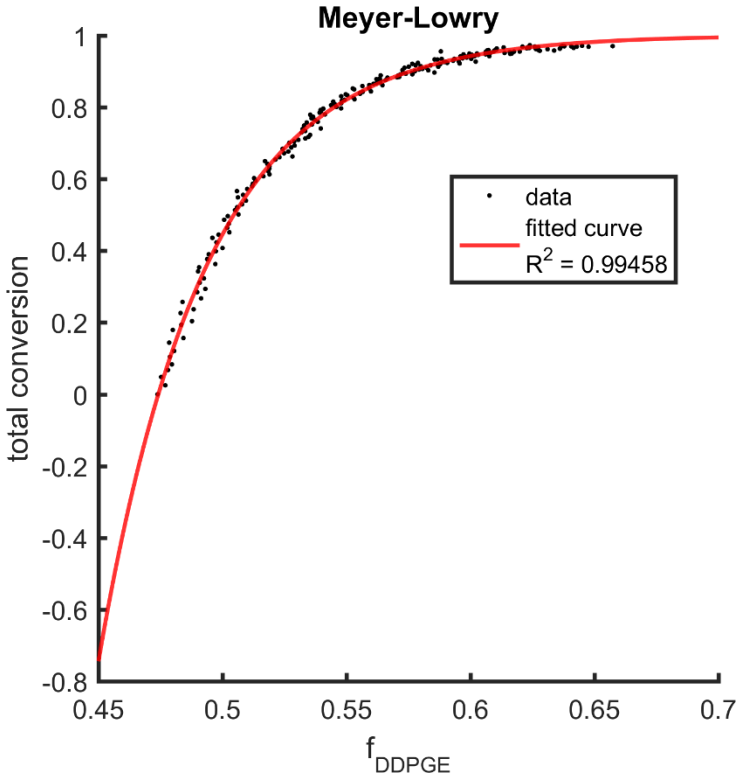

Figure S16. Meyer-Lowry fit of copolymerization of EO and DPPGE.

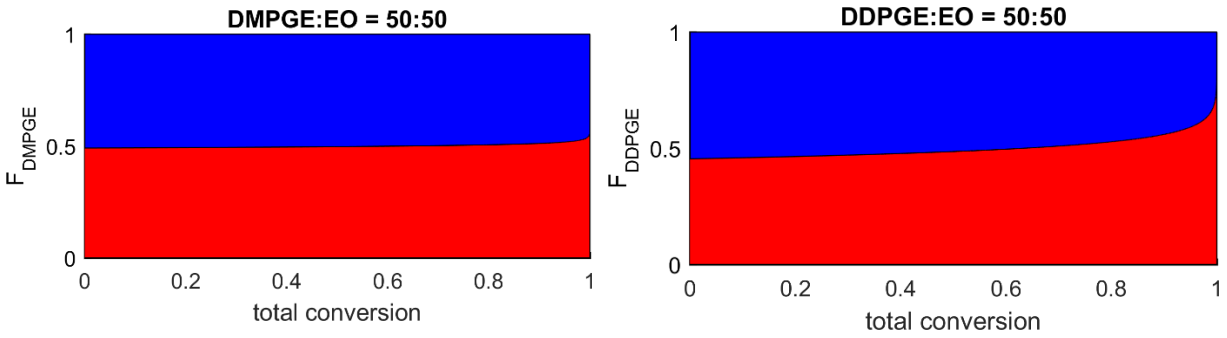

Figure S17. Simulation of the distribution of acetal functionalities for a 50:50 copolymer of EO with DMPGE (left) and DDPGE (right) in the polyether chain.

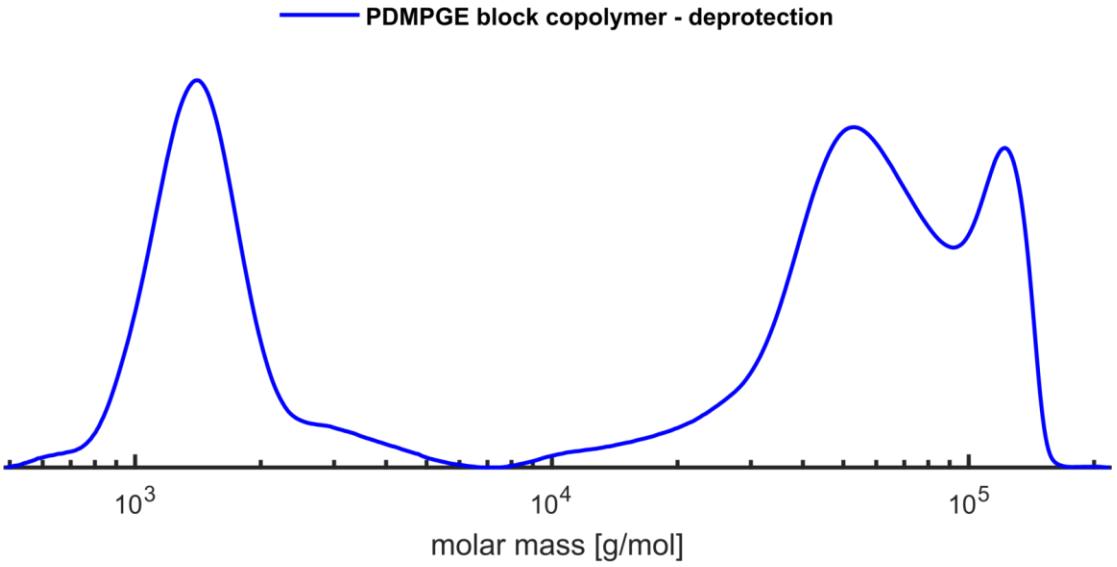

Figure S18: Crosslinking observed after deprotection of a PDMPGE block copolymer in SEC (DMF, PEG-calibration).

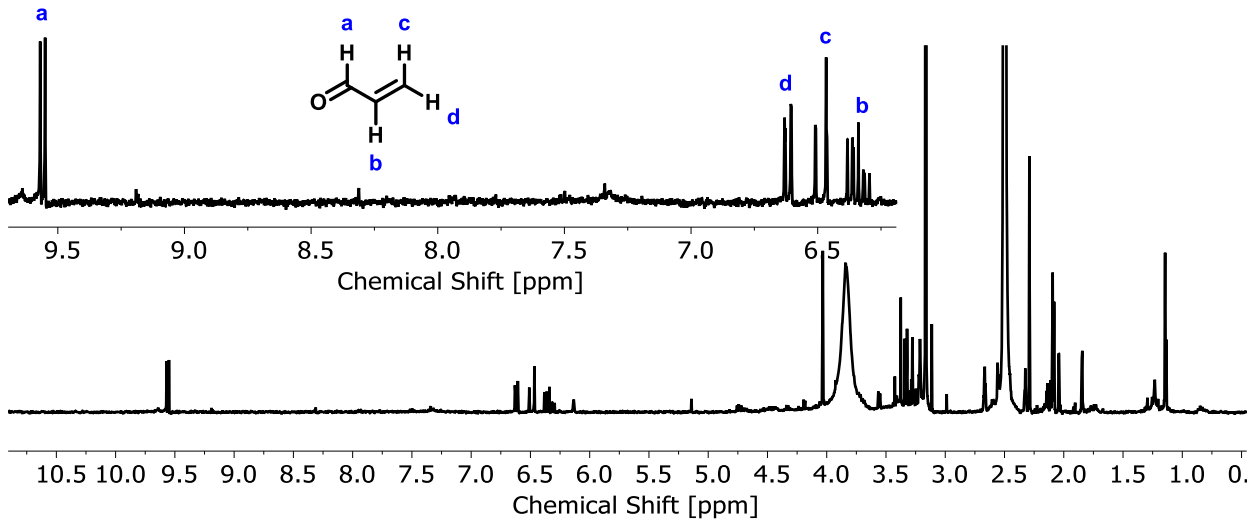

Figure S19. ^{1}H NMR (400 MHz, DMSO-*d*6) shows the formation of acrolein at deprotection attempt of PDMPGE$_7$ homopolymer.

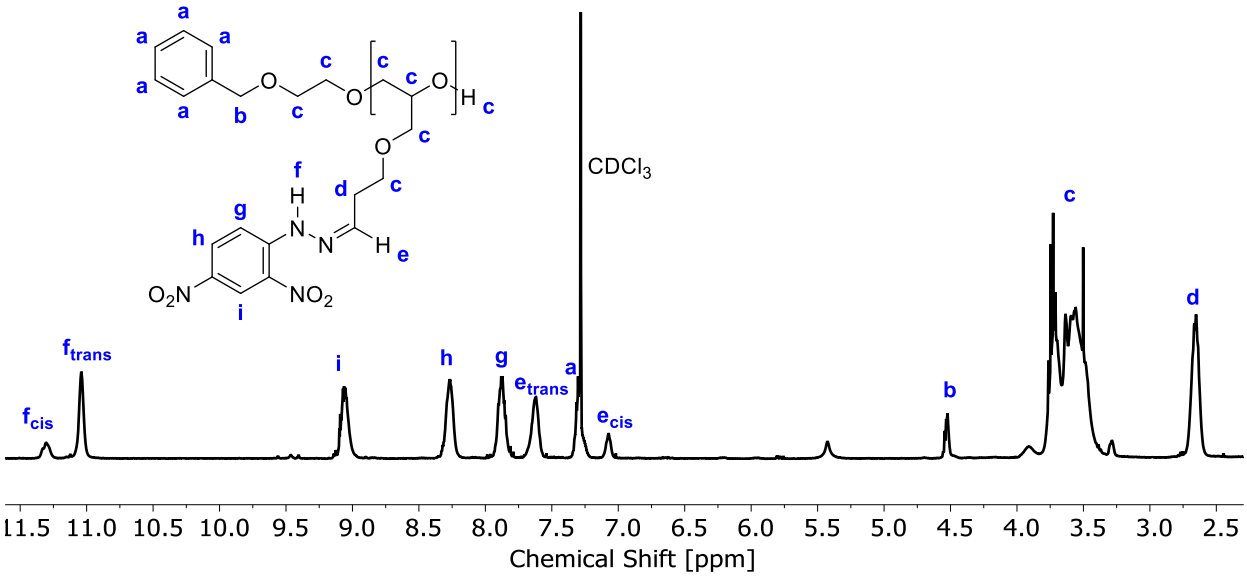

Figure S20. ^{1}H NMR (400 MHz, C*D*Cl$_3$) of the hydrazone modified P(DMPGE)$_7$ homopolymer.

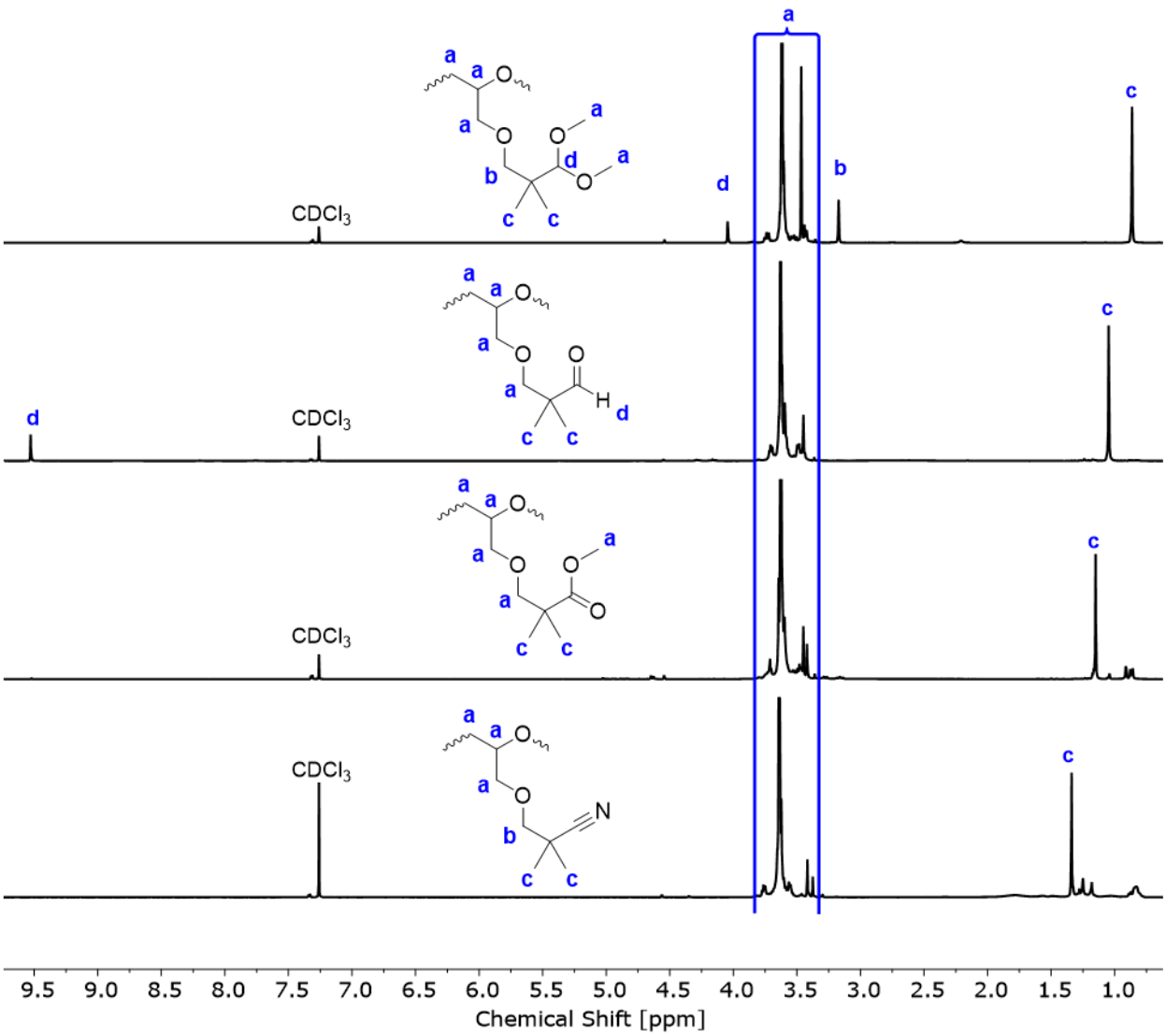

Figure S21: ^{1}H NMR (400Mhz, C*D*Cl$_3$) spectra of acetal, aldehyde, methyl ester and nitril-functional PEG.

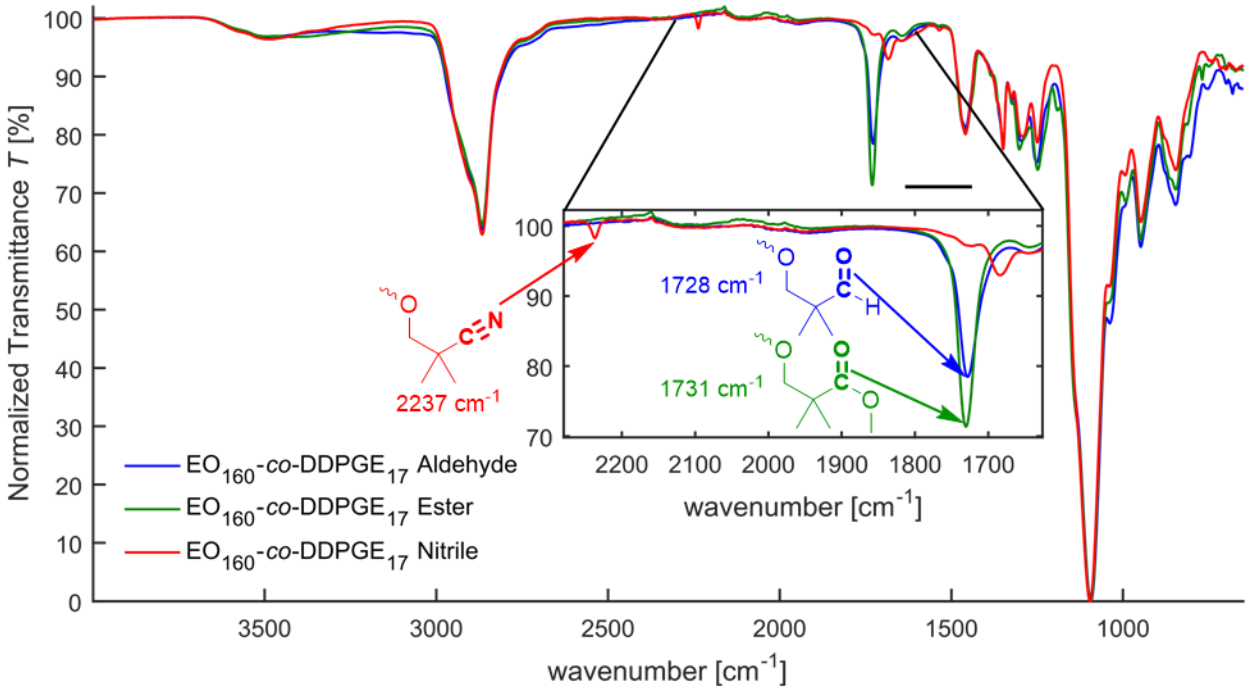

Figure S22: IR-spectra of post-polymerization reactions with assigned vibration bands.

Figure S23. Positive Angeli-Rimini[2] chemical test of aldehyde functional PEG. The red-colored hydroxamic acid complexes could be partly transferred to the bottom dichloromethane layer.

References (SI)

(1) Blankenburg, J.; Wagner, M.; Frey, H. Well-Defined Multi-Amino-Functional and Stimuli-Responsive Poly(propylene oxide) by Crown Ether Assisted Anionic Ring-Opening Polymerization. *Macromolecules* **2017**, *50*, 8885–8893, DOI: 10.1021/acs.macromol.7b01324.

(2) Gattermann, L.; Wieland, H.; McCartney, W. *Laboratory methods of organic chemistry*; Macmillan, 1937.