- Supporting Information –

Epicyanohydrin: Polymerization by Monomer Activation Gives Access to Nitrile, Amino and Carboxyl-Functional Poly(ethylene glycol)

Jana Herzberger,[a,b] *Holger Frey* [a,*]

[a] Department of Organic Chemistry, Johannes Gutenberg-University Mainz, Duesbergweg 10-14, 55128 Mainz, Germany

[b] Graduate School Materials Science in Mainz, Staudingerweg 9, 55128 Mainz, Germany

*E-Mail: hfrey@uni-mainz.de

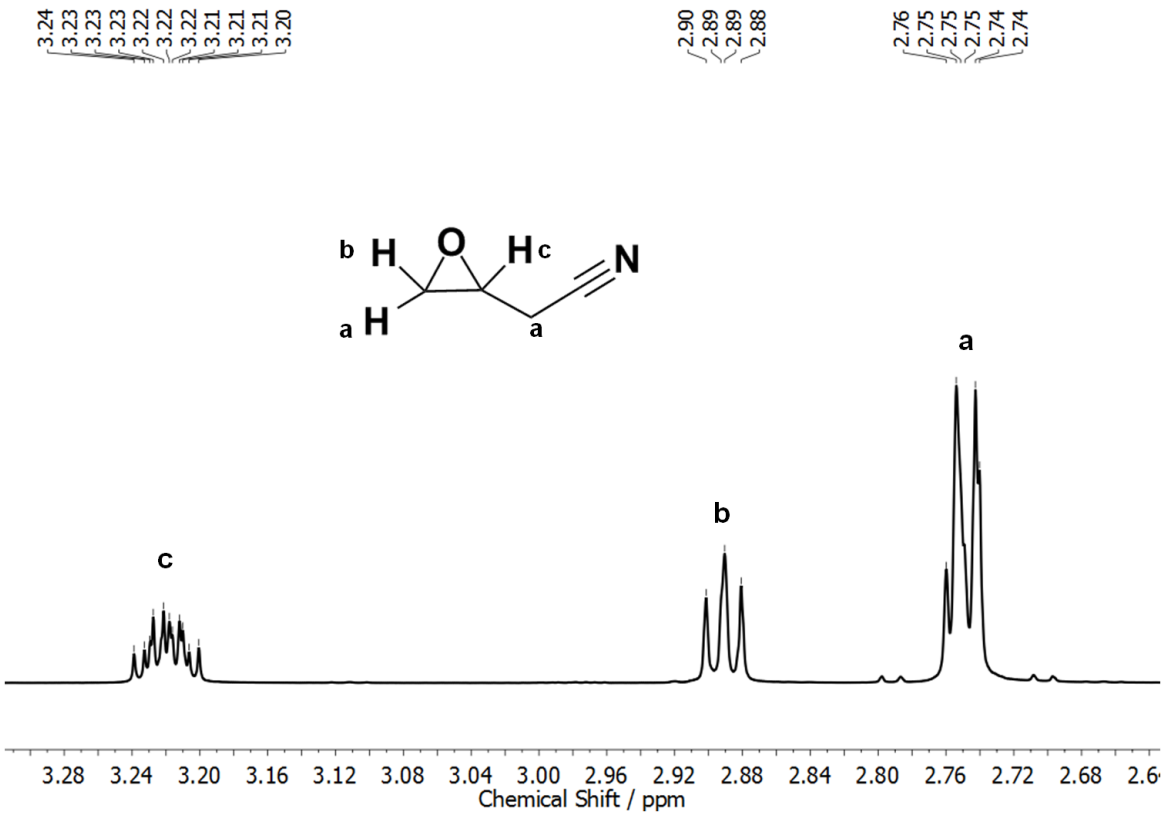


Figure S1. ^{1}H NMR spectrum (400 MHz, C*D*Cl$_3$) of epicyanohydrin (EPICH).

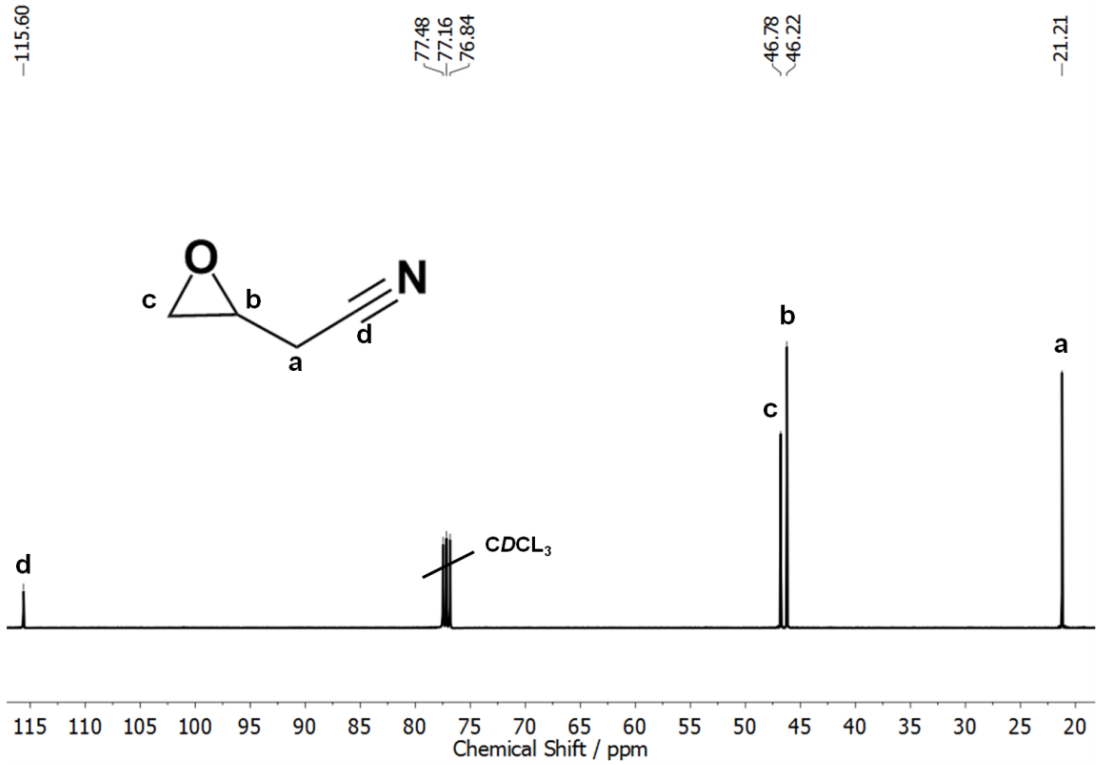


Figure S2. ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of EPICH.

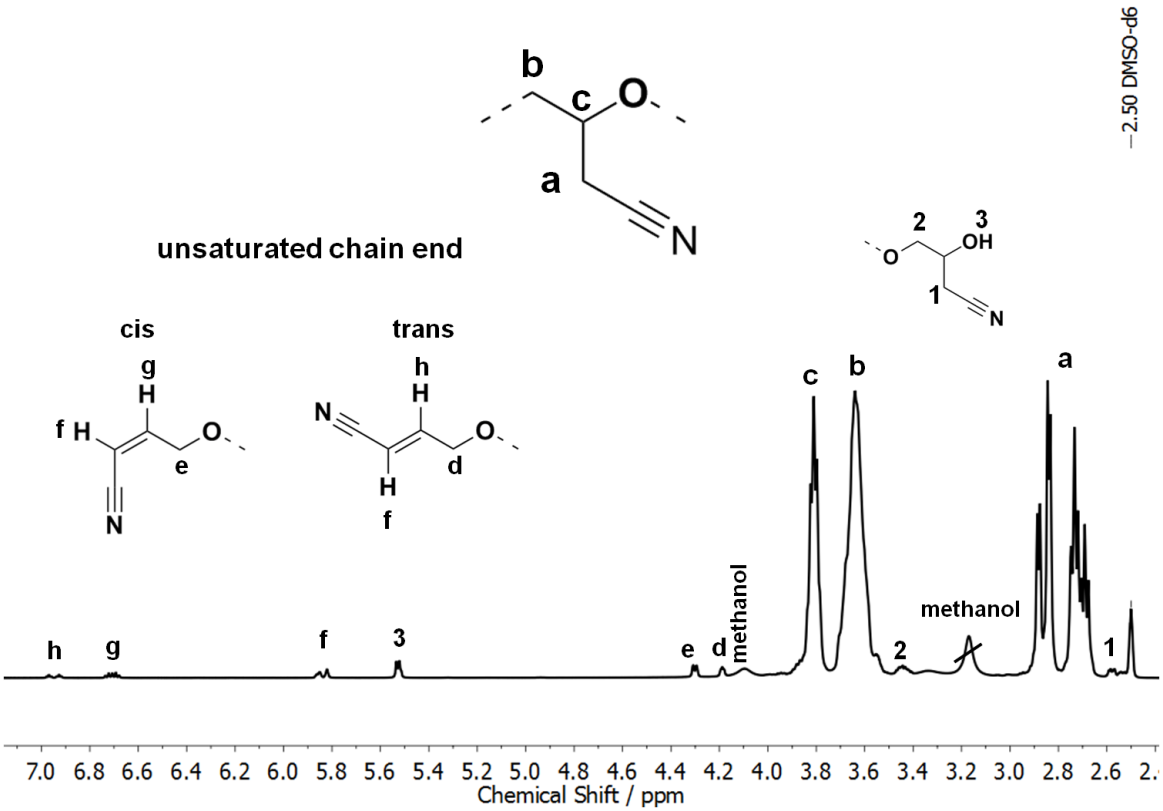


Figure S3. ^{1}H NMR spectrum (400 MHz, DMSO-d_6) of PEPICH homopolymer.

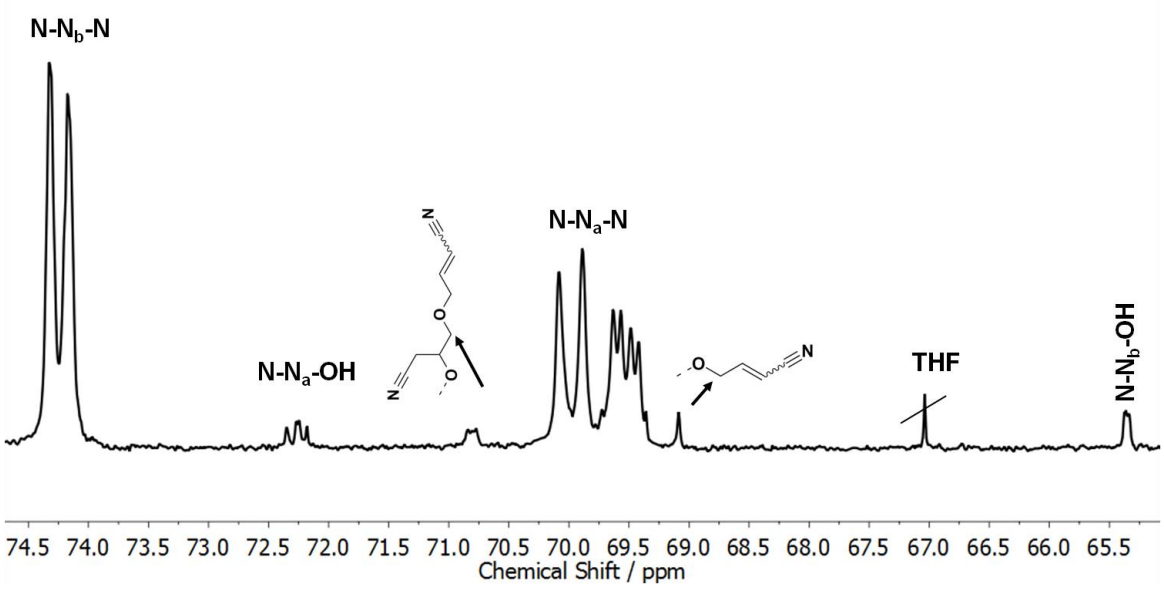


Figure S4. Important section of the IG ^{13}C NMR spectrum (100 MHz, DMSO-d_6) of PEPICH homopolymer; "N" is an abbreviation for the EPICH unit.

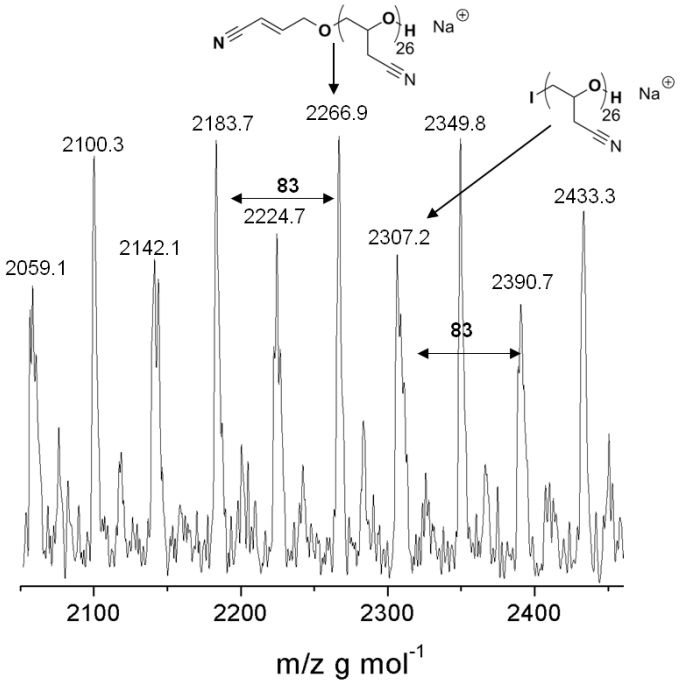


Figure S5. Expanded MALDI-ToF mass spectrum of $PEPICH_{26}$ with peak assignment (linear mode, matrix: THAP). One repeating unit of EPICH (83 g·mol^{-1}) is marked by black arrows. Main distributions correspond to the sodium adduct of $PEPICH_{26}$, initiated via iodide and unsaturated species, respectively.

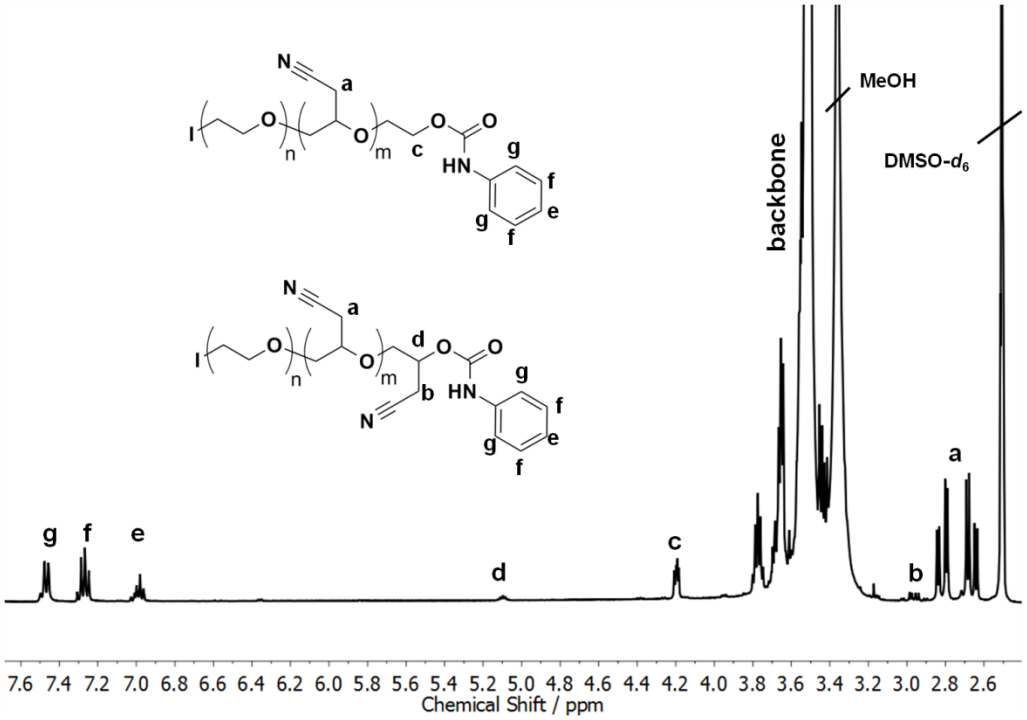
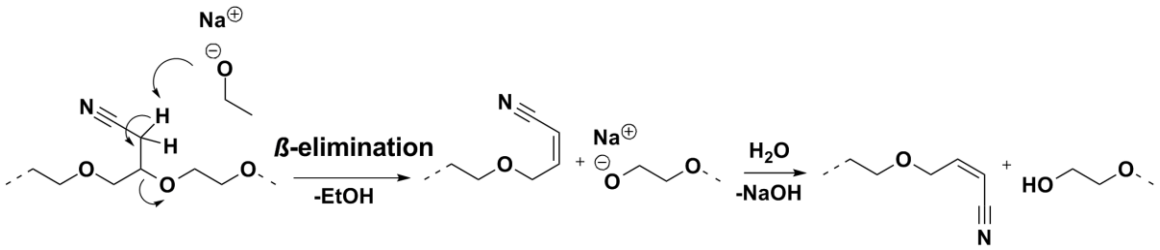


Figure S6. ^{1}H NMR (400 MHz, DMSO-d_6) of PEG-*co*-PEPICH copolymer, functionalized with phenyl isocyanate.



Scheme S1. *β*-elimination (Retro-Michael addition), exemplarily shown for an E-N-E triad and resulting cleavage of the PEG-*co*-PEPICH backbone.

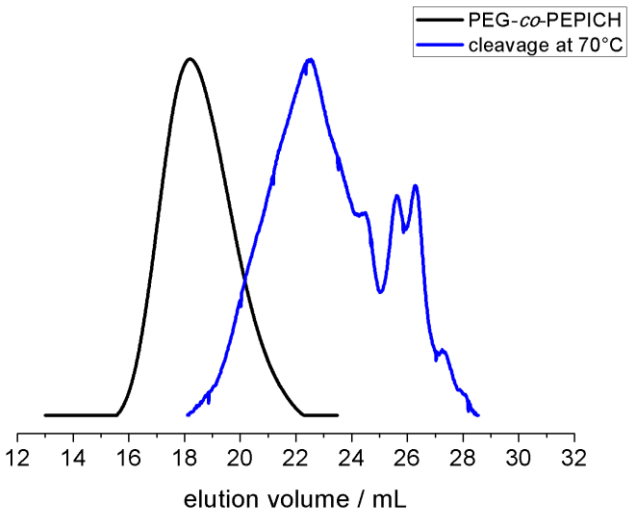


Figure S7. SEC elution traces (DMF, RI detection, PEG standards) of PEG-*co*-PEPICH copolymer (7 mol% EPICH) before cleavage (black line) and after cleavage at 70 °C (blue line).

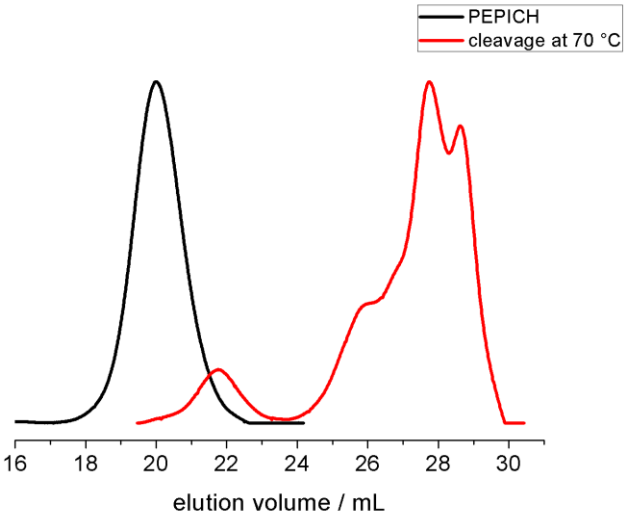


Figure S8. SEC elution traces (DMF, RI detection, PEG standards) of PEPICH homopolymer before cleavage (black line) and after cleavage at 70 °C (red line).

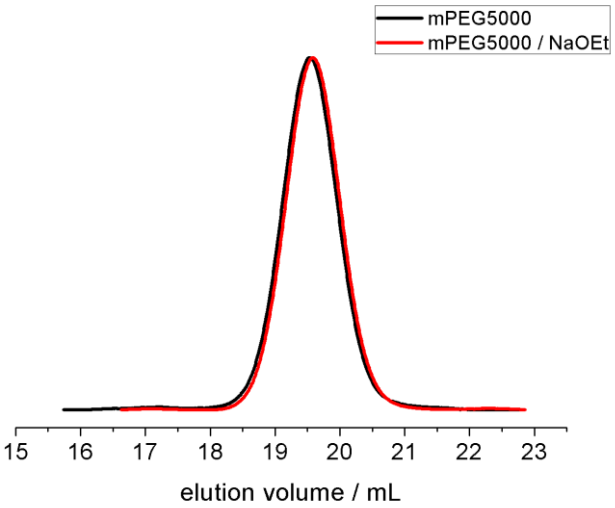
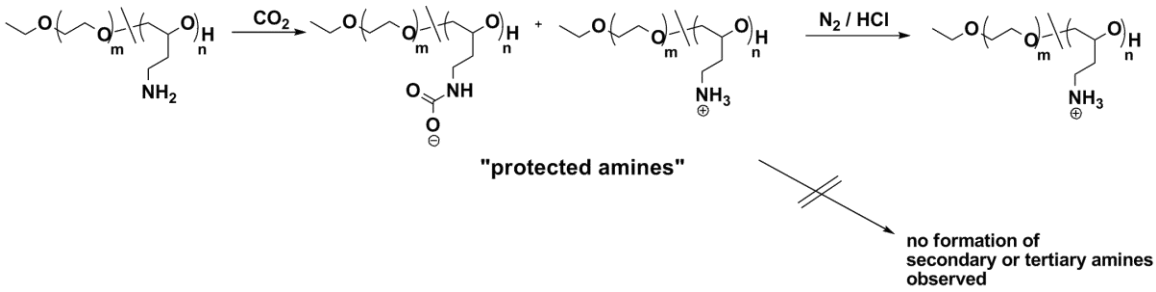


Figure S9. SEC elution traces (DMF, RI detection, PEG standards) of mPEG5000 before cleavage (black line) and after treatment with sodium ethoxide solution at 70 °C (red line).



Scheme S2. Reaction of amino moieties with carbon dioxide to ammonium carbamates, followed by release of the amino groups *via* N_2/HCl.

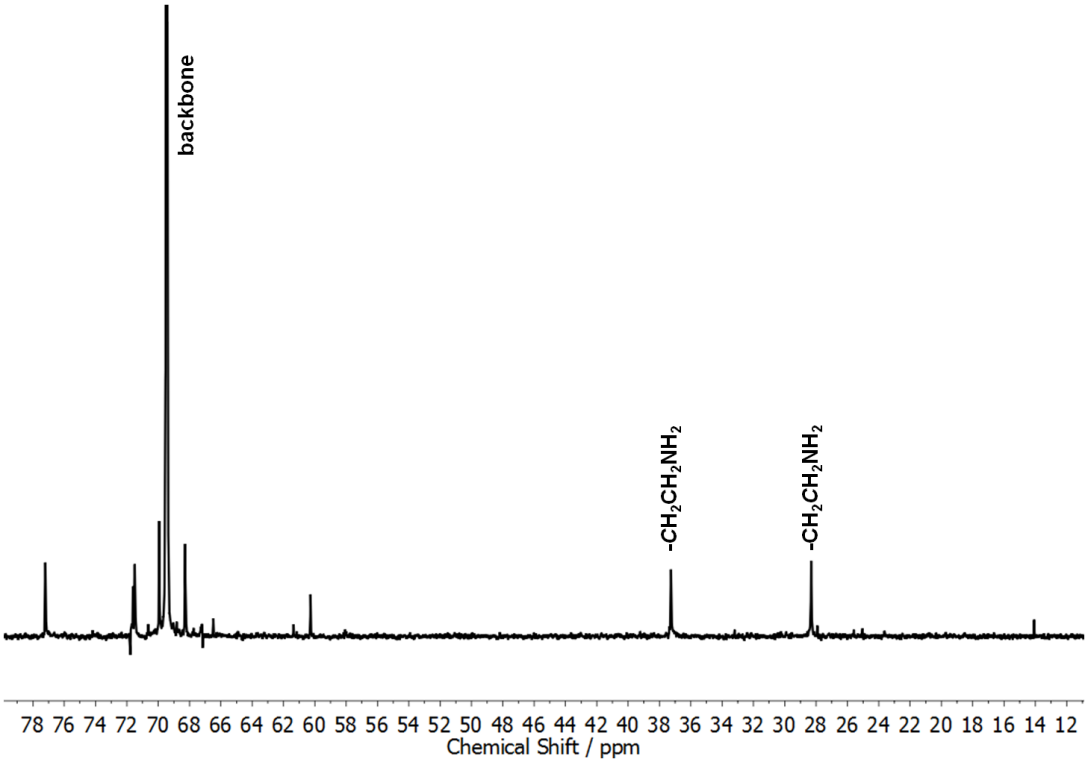


Figure S10. ^{13}C NMR (100 MHz, D_2O) of PEG-*co*-POEA with 6.1 % OEA.

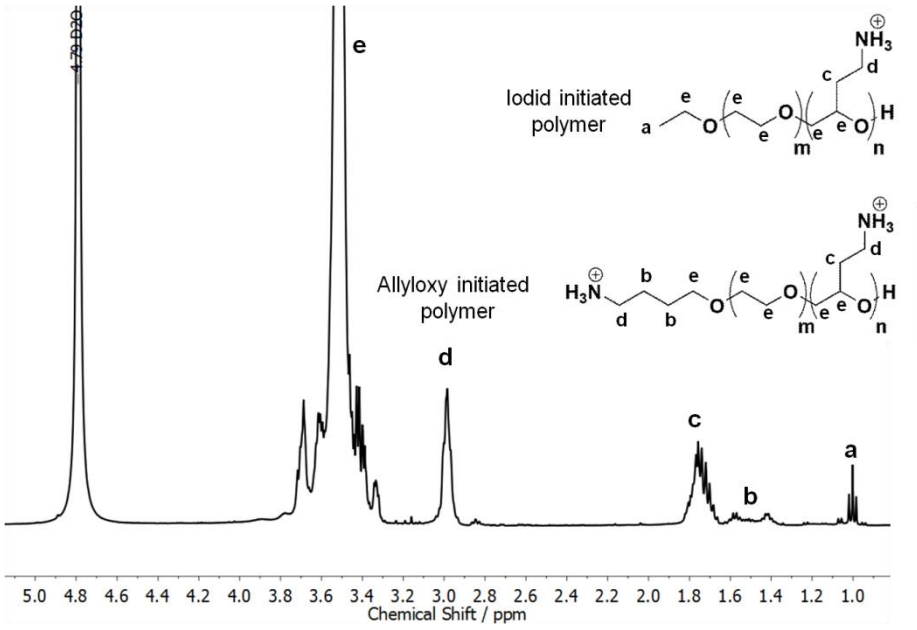


Figure S11. ^{1}H NMR spectrum (400 MHz, D_2O) of PEG-*co*-POEA with 6.1 % OEA.

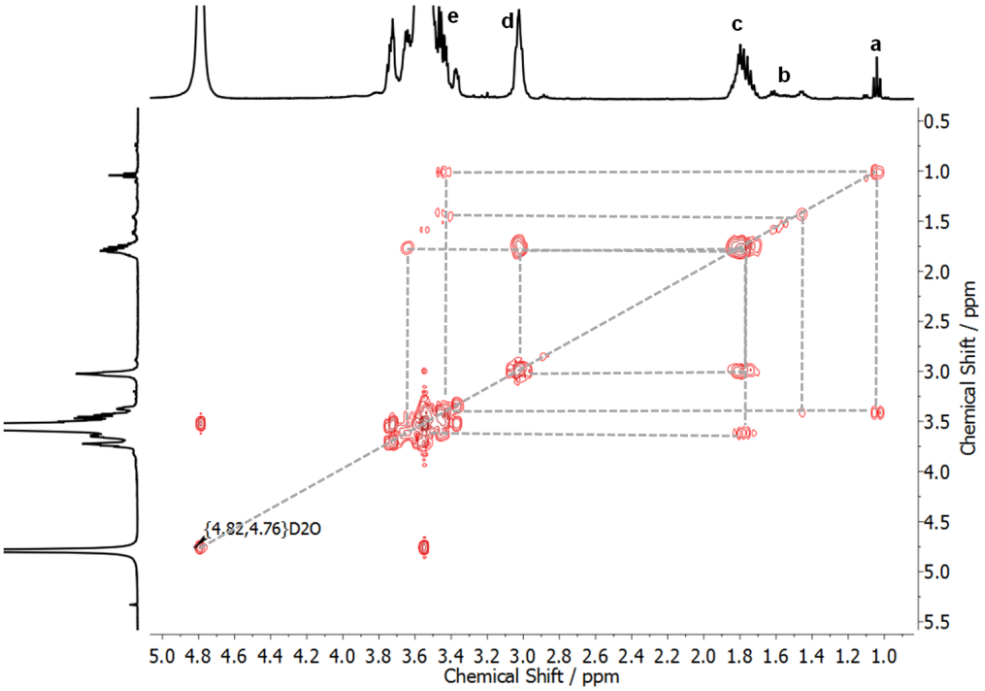


Figure S12. ^{1}H, ^{1}H COSY NMR (400 MHz, D_2O) of PEG-*co*-POEA with 6.1 % OEA.

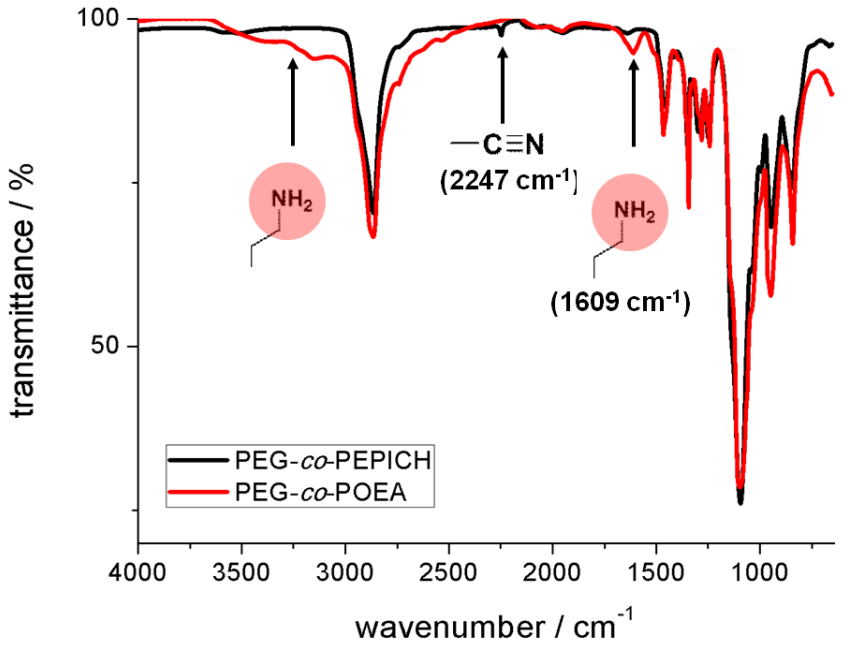


Figure S13. FT-IR spectra of PEG-*co*-PEPICH (black line) and amino-functional PEG-*co*-POEA (red line).

Table S1. Thermal properties of PEG-*co*-PEPICH and PEG-*co*-POEA obtained from differential scanning calorimetry (DSC) measurements.

Copolymer	[a]FG content / %	T_g/°C	T_m/°C	T_{rc} / °C	ΔH/J·g^{-1}
PEG-*co*-PEPICH	3.8	-48	44	---	87
PEG-*co*-POEA	3.8	-43	44	---	78
PEG-*co*-PEPICH	6.1	-49	36	---	58
PEG-*co*-POEA	6.1	-40	36	---	61
PEG-*co*-PEPICH	7.7	-48	28	---	63
PEG-*co*-POEA	7.7	-44	34	-13	47
PEG-*co*-PEPICH	13.1	-52	5	-11	20
PEG-*co*-POEA	13.1	-27	---	---	---
PEG-*co*-PEPICH	16.0	-46	---	---	---
PEG-*co*-POEA	16.0	-22	---	---	---

[a]FG = functional group
T_g: glass transition temperature
T_m: melting temperature
ΔH: melting enthalpy

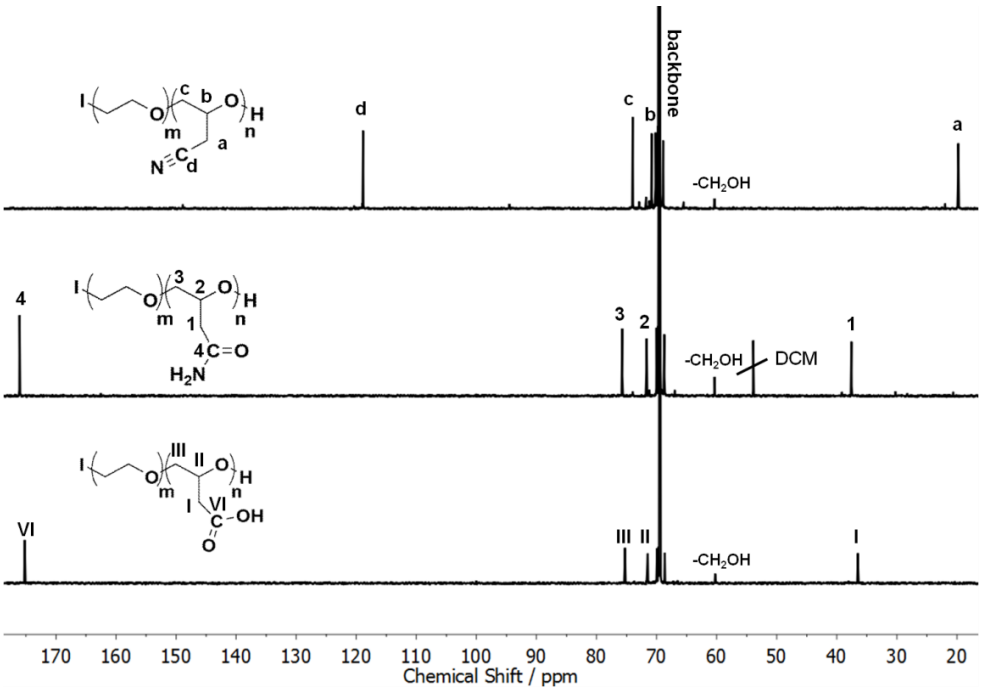


Figure S14. ^{13}C NMR spectra (100 MHz, D_2O) of PEG-*co*-PEPICH (top), PEG-*co*-POAm and PEG-*co*-POAa (bottom), respectively.

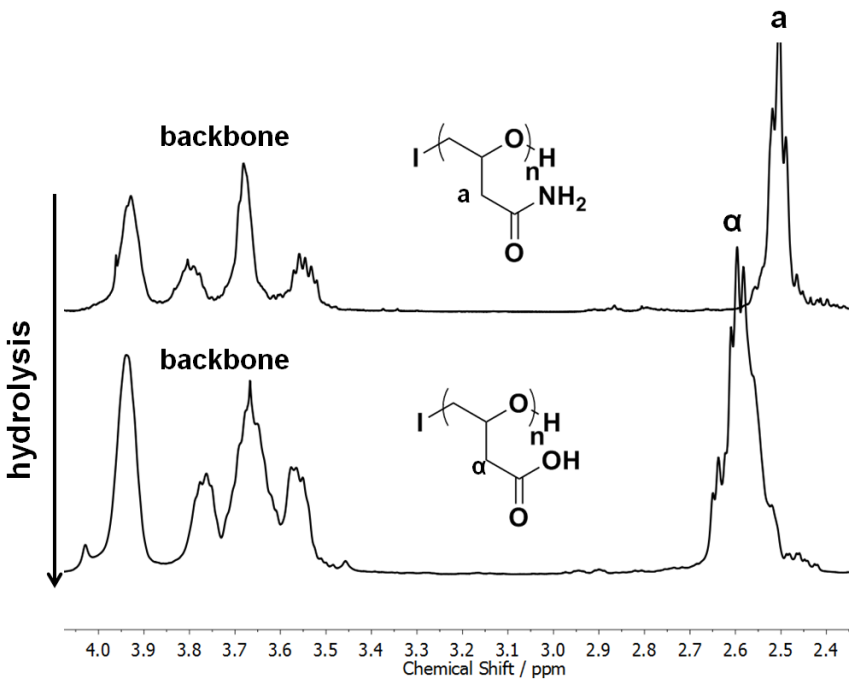


Figure S15. Important sections of ^{1}H NMR spectra (400 MHz, D_2O) of poly(2-oxiraneacetamide) (POAm) (top) and poly(2-oxiraneacetic acid) (POAa) (bottom).

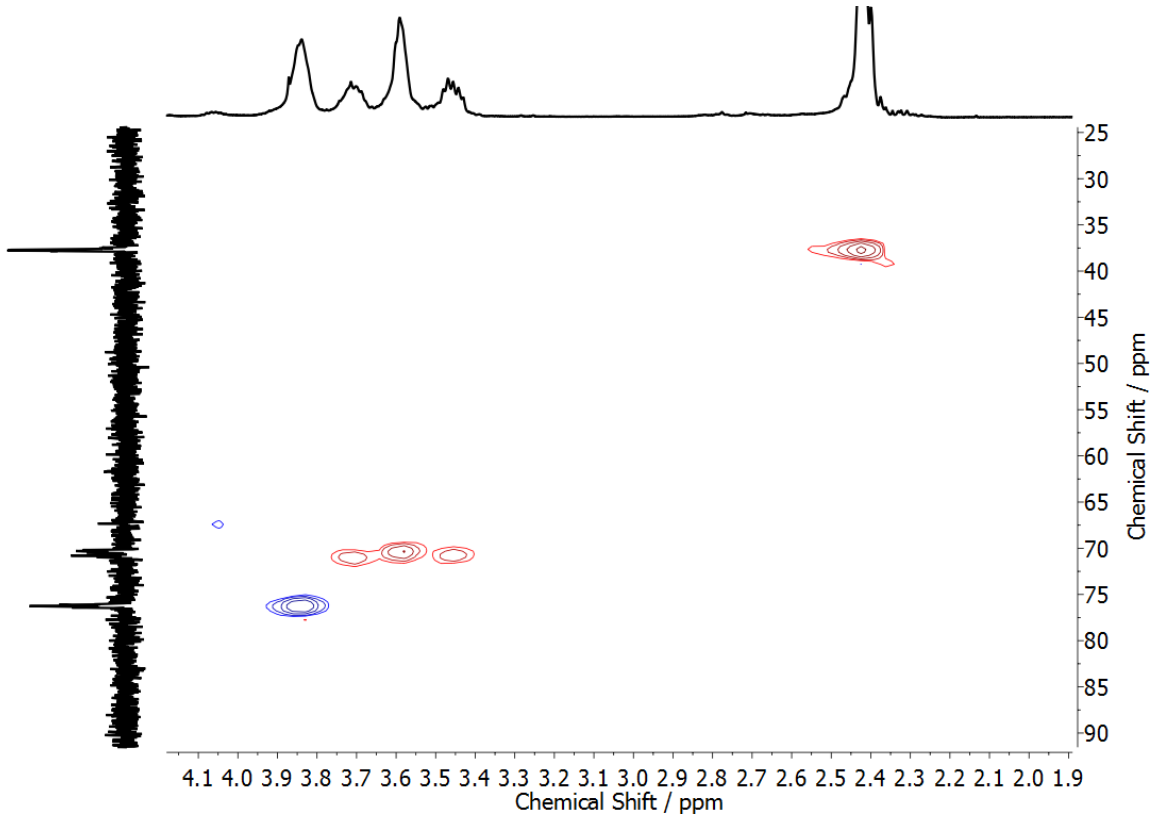


Figure S16. ^{1}H- ^{13}C-HSQC NMR spectrum (D_2O) of poly(2-oxiraneacetamide). Phase information is given by coloration of cross peaks (red: methylene, blue: methine).

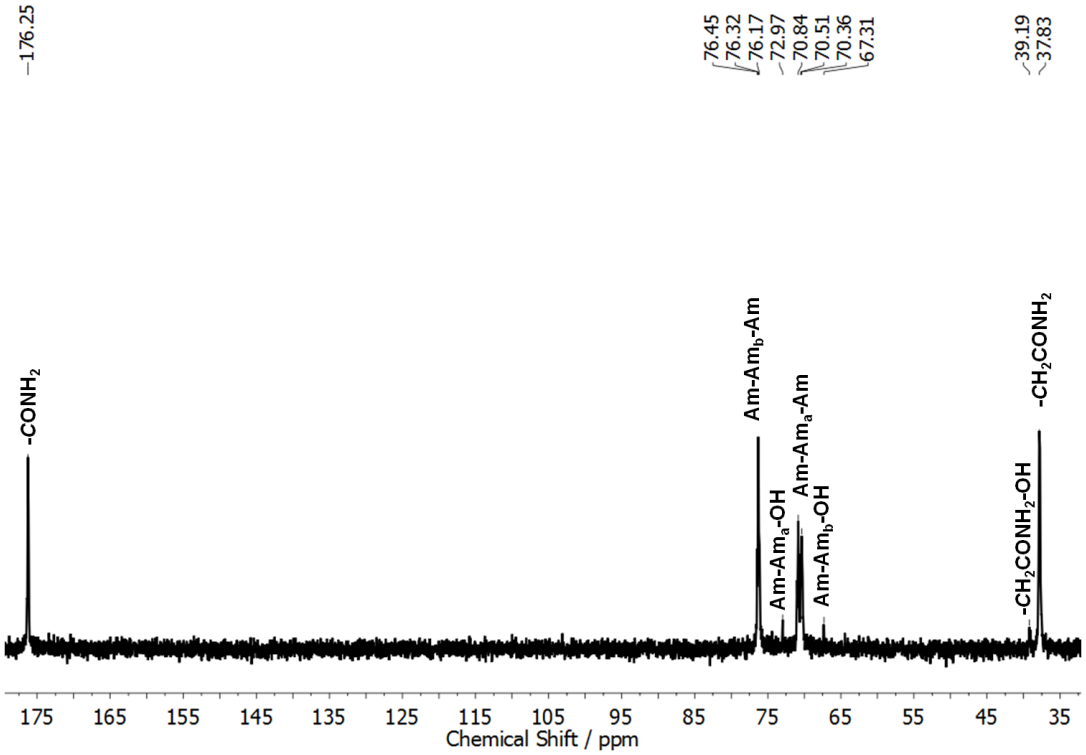


Figure S17. ^{13}C NMR spectrum (100 MHz, D_2O) of poly(2-oxiraneacetamide) homopolymer. 2-oxiraneacetamide unit is abbreviated as "Am".

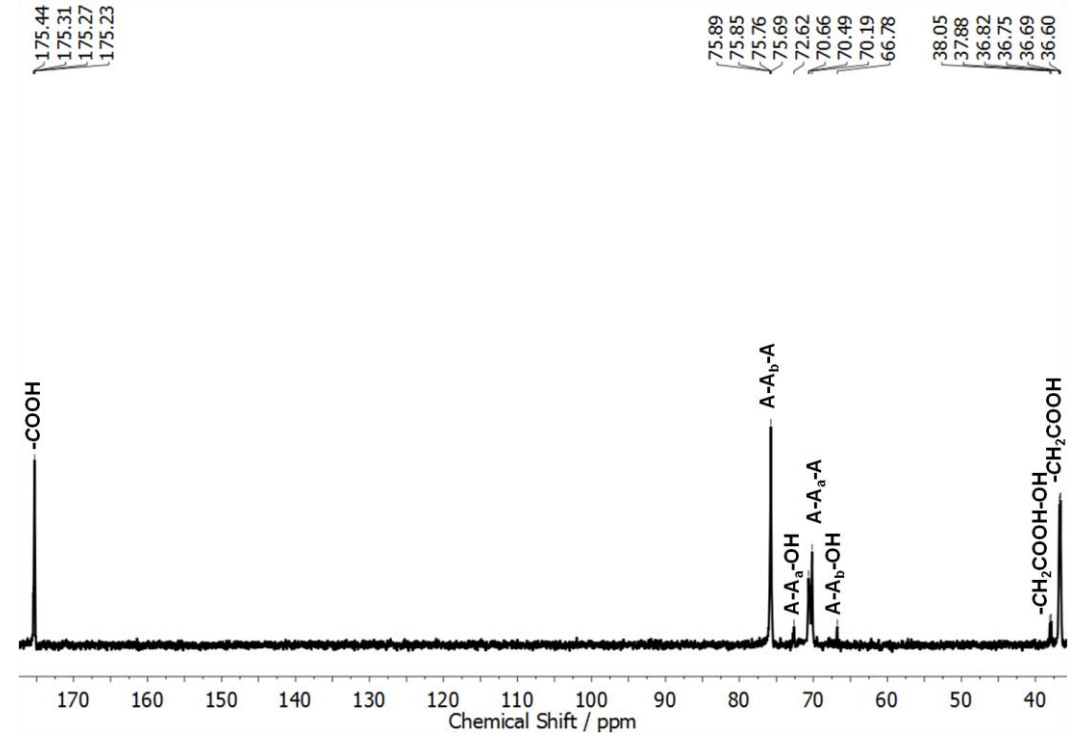


Figure S18. ^{13}C NMR spectrum (100 MHz, D_2O) of poly(2-oxiraneacetic acid) homopolymer. 2-oxiraneacetic acid unit is abbreviated as "A".

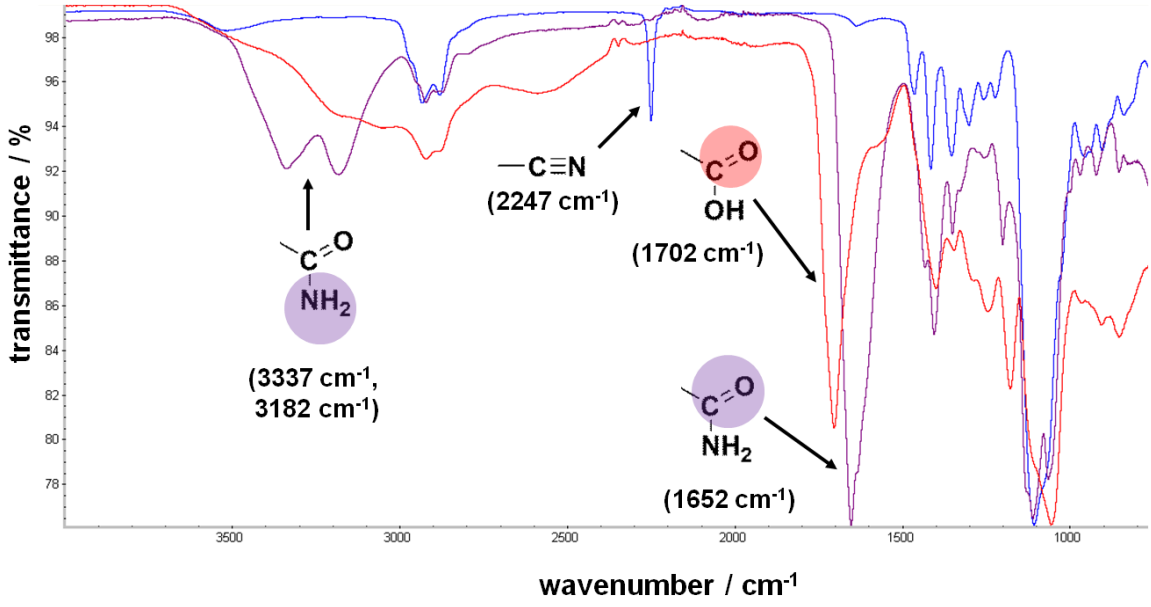


Figure S19. FT-IR spectra of PEPICH (blue line), POAm (violet line) and POAa (red line).

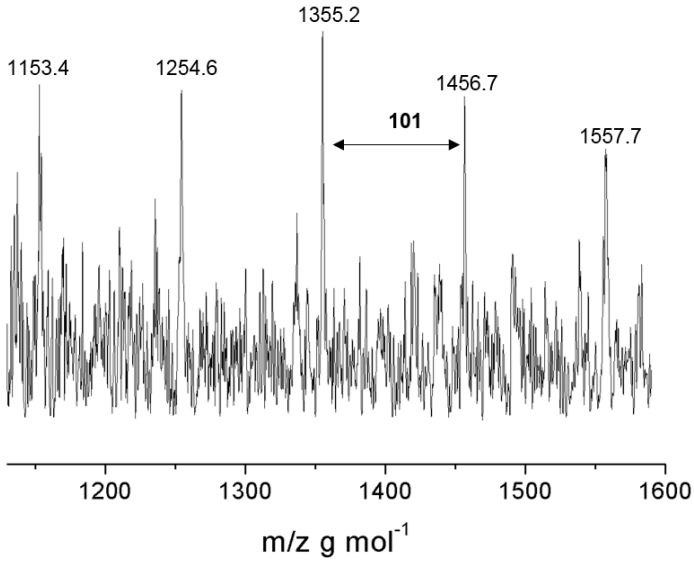


Figure S20. Expanded MALDI-ToF mass spectrum of amide functional POAm homopolymer (linear mode, matrix: THAP). The repeating unit difference for OAm (101 g·mol^{-1}) is marked by a black arrow.

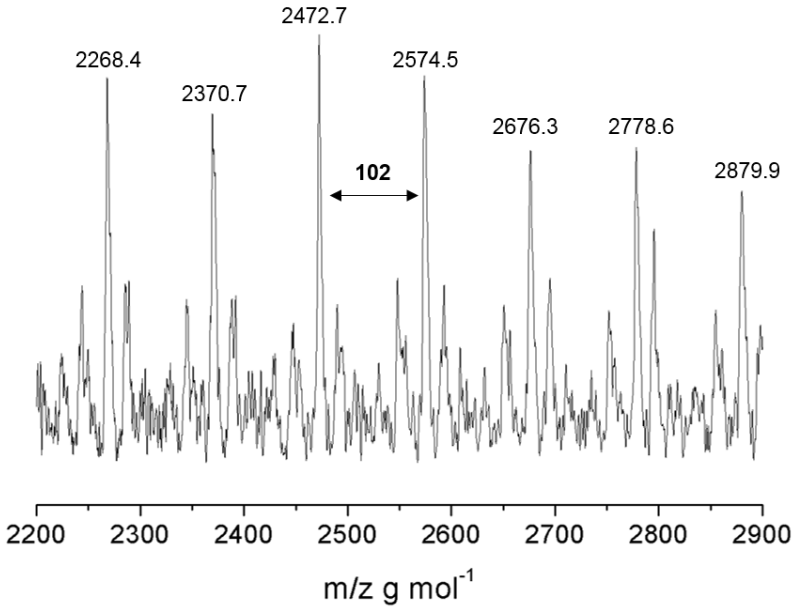


Figure S21. Expanded MALDI-ToF mass spectrum of carboxyl functional POAa homopolymer (linear mode, matrix: THAP). The repeating unit mass difference for OAa (102 g·mol^{-1}) is marked by a black arrow.

Table S2. Thermal properties of PEG-*co*-PEPICH, PEG-*co*-POAm and PEG-*co*-POAa copolymers obtained from differential scanning calorimetry (DSC) measurements.

Copolymer	[a]FG content / %	T_g/°C	T_m/°C	T_{rc} / °C	ΔH/J·g^{-1}
PEG-*co*-PEPICH	3.8	-48	44	---	87
PEG-*co*-POAm	3.8	-48	38	-27	57
PEG-*co*-POAa	3.8	-37	42	---	71
PEG-*co*-PEPICH	6.1	-49	36	---	58
PEG-*co*-POAm	6.1	-48	32	-24	53
PEG-*co*-POAa	6.1	-55	29	-37	63
PEG-*co*-PEPICH	7.7	- 48	28	---	63
PEG-*co*-POAm	7.7	-48	29	-23	53
PEG-*co*-POAa	7.7	-52	28	-32	60
PEG-*co*-PEPICH	13.1	-52	5	-11	20
PEG-*co*-POAm	13.1	-40	---	---	---
PEG-*co*-POAa	13.1	-45	---	---	---
PEG-*co*-PEPICH	16.0	-46	---	---	---
PEG-*co*-POAm	16.0	-30	---	---	---
PEG-*co*-POAa	16.0	-36	---	---	---
PEPICH	100	-14	---	---	---
POAm	100	55	---	---	---
POAa	100	29	---	---	---

[a]FG = functional group
T_g: glass transition temperature
T_m: melting temperature
ΔH: melting enthalpy