Supporting Information

Biobased Oleyl Glycidyl Ether: Copolymerization with Ethylene Oxide, Postmodification, Thermal Properties, and Micellization Behavior

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Experimental Section

Reagents

The chemicals were sourced from commercial suppliers, such as *Sigma-Aldrich, TCI*, *Fluka*, and *Acros*, and were used without purification unless otherwise specified. The deuterated solvents were obtained from *Deutero GmbH* (Germany). Oleic acid methyl ester (99% purity) was procured from *Sigma-Aldrich*. Ethylene oxide (EO) was purchased from *Air Liquide*. Oleyl glycidyl ether (OlGE) was dried overnight using benzene under a high vacuum prior to polymerization. [18]Crown-6 was dried by azeotropic distillation under high vacuum, dissolved in a defined amount of dry benzene in a flame-dried Schlenk flask, and stored under argon. DMSO was stored over molecular sieves and added to the initiator salt using a syringe. Tetrahydrofuran (THF) was dried over a mixture of butyllithium and diphenylethylene, degassed, and stored under vacuum. The mixture was then transferred to the polymerization flask using cryogenic techniques. For online ^{1}H NMR kinetics, deuterated THF (THF-d_8) was dried over CaH_2 overnight and subsequently cryogenically transferred. DMSO-d_6 from a fresh bottle was used. Uranyl acetate solution for negative staining in transmission electron microscopy was purchased from *Polyscience*. The carbon-coated copper grids with 400 mesh (CF-400-Cu) were acquired from *Electron Microscopy Sciences*.

Instrumentation

Nuclear Magnetic Resonance (NMR) Spectroscopy

Standard 300 MHz NMR measurements were performed on a *Bruker Avance III HD 300* equipped with a 5 mm BBFO probe head with *z*-gradient and ATM. Standard 400 MHz NMR spectra were measured on a *Bruker Avance II 400* spectrometer with a 5 mm BBFO probe head with *z*-gradient and ATM. The spectra are referenced internally to the residual proton signal (^{1}H NMR) of the signal of the naturally occurring ^{13}C atom in the respective solvent (^{13}C NMR).

Two-dimensional- NMR Experiments, such as COSY, HSQC, DOSY, and HMBC, as well as *in situ* ^{1}H NMR copolymerization kinetics, were performed on a *Bruker Avance III 400* with a 5 mm BBO cryo probe

head (BB/H+F), which was cooled with liquid nitrogen, with *z*-gradient, and ATM. All spectra were acquired at 23 °C unless stated otherwise and processed using *MestReNova* 14.3.32681.

Size Exclusion Chromatography (SEC)

SEC analysis using *N*,*N*-dimethylformamide (DMF) as the eluent was performed using an *Agilent 1100 series* SEC system. The system was equipped with UV- (254 nm) and RI detectors, and a HEMA 300/100/40 Å column cascade was used. The measurements were conducted at a flow rate of 1 mL/min, with DMF as an eluent, containing 1 g/mL lithium bromide at a temperature of 50 °C. SEC analysis with THF as the eluent was conducted using a MZ-Gel SD plus e5/e3/100 column cascade, *P100* pump, and *Waters 717 plus* injector. The SEC system was equipped with UV- (254 nm) and refractive index (RI) detectors. The eluent flow rate was set to 1 mL/min. Toluene was used as the internal standard in both cases. The SEC calibration was performed using poly(ethylene glycol) standards provided by *Polymer Standard Service* (*PSS*). Data recording and processing were performed using the *PSS WinGPC UniChrom* software.

Matrix-assisted Laser Desorption Ionization Time-of-Flight (MALDI-ToF) Mass Spectrometry

MALDI-ToF analysis was performed using a *Bruker autoflex maX MALDI-ToF-MS/MS* instrument in linear or reflector mode. The analysis was conducted on a multi-target plate. *trans*-2-[3-(4-*tert*-Butylphenyl)-2-methyl-2-propenylidene] malononitrile (DCTB) or Dithranol (Dit) were used as the matrix. Potassium trifluoroacetate (KTFA) was used as a salt additive.

Differential Scanning Calorimetry (DSC)

DSC measurements were conducted using a *TA Instruments DSC 250* instrument equipped with a *Recovery Cooling System 90*. The measurements were conducted under a dry nitrogen flow at a rate of 20 mL/min. The instrument was calibrated using indium and *n*-octane as standards. Before analysis, all samples were dried by azeotropic distillation with benzene and weighed in aluminum pans with pinholes. The heating and cooling steps during the measurement were as follows.

1) Cool to -90 °C with 10 K/min, and hold for 5 min.

2) Heat to 100 °C with 10 K/min, and hold for 5 min.
3) Cool to -90 °C with 10 K/min, and hold for 5 min.
4) Heat to 100 °C with 10 K/min, and hold for 5 min.

Additionally, Steps 3 and 4 were repeated at a slower rate of 1 K/min in a separate run. All the reported physical values were extracted from the second heating cycle to ensure removal of the thermal history of the sample.

Transmission Electron Microscopy (TEM)

TEM images were acquired using an *FEI Tecnai G2 12 BioTwin* electron microscope operating at an acceleration voltage of 120 kV with a LaB6 cathode emitter. The microscope was equipped with two cameras: an on-axis *4kx4k Tietz CMOS* camera and a side-entry *MegaSYS 1kx1k CCD* camera.

Prior to imaging, carbon-coated copper grids with 400 mesh (CF-400-Cu) were hydrophilized using a plasma cleaner for one minute. Subsequently, 20 µL of the sample solution (0.1 g/L) was added to the grid and incubated for one minute. After the incubation period, excess liquid was removed by gently blotting the grid with filter paper. To enhance the contrast, 20 µL of uranyl acetate solution (2%) was added to the grid and blotted with filter paper after one minute.

Importantly, all the prepared grids were immediately investigated on the same day, as their preparation to ensure the integrity and consistency of the sample during imaging.

CMC determination by fluorescence spectroscopy

Polymer solutions were prepared using stock solutions at concentrations of 1 g/L, 0.1 g/L, and 0.01 g/L, with Milli-Q® water as the solvent. Pyrene, dissolved in ethanol (Uvasol®), was introduced into empty graduated flasks, aiming for a final concentration of $7 \cdot 10^{-7}$ mol/L. The ethanol was subsequently evaporated, and the desired concentration was achieved by adding an appropriate volume of polymer stock solution along with Milli-Q® water. The flasks were gently agitated overnight on a laboratory shaker at room temperature to facilitate the equilibration of both pyrene and the micelles. Emission spectra were captured using a *Jasco FP-8200* spectrofluorometer with an excitation wavelength of

335 nm. The range covered 350–450 nm, with a data interval of 0.5 nm and a scanning rate of 20 nm/min. The excitation bandwidth was 2.5 nm, and the emission bandwidth was 2.5 nm. Quartz cells with a path length of 10 mm were employed for the solutions and were pre-treated with the corresponding polymer solution once. The data obtained from plotting the intensity ratio between the first (I_1) and third (I_3) vibronic bands in the fluorescence spectrum of pyrene against the logarithmic concentration of the polymer were analyzed using a Boltzmann sigmoidal fit (equation (S1)).[1]

$$\frac{I_3}{I_1} = \frac{A_1 - A_2}{1 + e^{(log(c) - log(CMC))/dx}} + A_2 \qquad \text{(S1)}$$

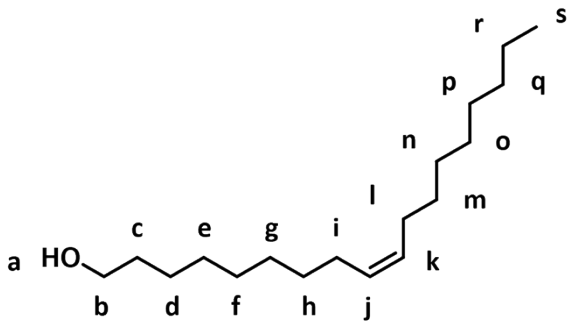
A_1 represents the lower boundary, while A_2 represents the upper boundary of the sigmoidal curve. The point of inflection denotes the logarithm of the CMC, and *dx* signifies the slope or steepness of the curve.

Monomer Synthesis

The monomer synthesis of oleyl glycidyl ether (OlGE) involved a two-step process that started with methyl oleate and led to the formation of oleyl alcohol. Subsequently, oleyl alcohol was subjected to phase-transfer catalysis using epichlorohydrin (ECH). Methyl oleate (purity of 99%) was purchased, because commercially available oleyl alcohol of comparable quality could not be obtained at a reasonable cost.

Synthesis of oleyl alcohol from methyl oleate

The reduction of methyl oleate to oleyl alcohol was performed following a standard organic synthesis procedure.[2] A 250 mL three-necked round-bottom flask, equipped with a Dimroth cooler (metal cooling coil), mechanical stirrer, and a dropping funnel, was thoroughly dried using a heat gun and purged with dry nitrogen. Diethyl ether (Et_2O, 84 mL), which was dried over sodium and freshly distilled, was added to the flask. Powdered lithium aluminum hydride (LAH, 1.76 g, 46.4 mmol, 0.55 eq.) was gradually added to the flask. Methyl oleate (25.00 g, 84.3 mmol, 1 eq.) was mixed with 24 mL of dry Et_2O and placed in a dropping funnel. The methyl oleate-Et_2O mixture was slowly added dropwise to the LAH suspension, maintaining a slightly boiling Et_2O. After complete addition, 50 mL of dry Et_2O was added and the resulting mixture was stirred overnight. Subsequently, ice-cold water was added dropwise, and the precipitate was dissolved by adding 10% sulfuric acid (H_2SO_4). The aqueous phase was extracted three times with 100 mL portions of petroleum ether. The combined organic phases were washed three times with brine and dried overnight with sodium sulfate. The solid was removed by filtration, and the solvents were evaporated. Column chromatography was performed using a stepwise solvent gradient. The eluent mixture of cyclohexane/ethyl acetate ranged from 4/1 to 1/20 (V_{Cy}/V_{EtOAc}) and yielded 21.87 g (81.5 mmol) of colorless liquid as the sum of four columns, corresponding to a yield of 97%.



Yield: 97%

Purification by column chromatography, R_F=0.4, eluent 4/1 (V_{cy}/V_{EtOAc})

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.39 – 5.26 (m, 2H, H_j, H_k), 3.60 (t, J = 6.7 Hz, 2H, H_b), 2.04 – 1.95 (m, 4H, H_i, H_l), 1.60 – 1.48 (m, 2H, H_c), 1.39 – 1.18 (m, 22H, H_{d-h}, H_{m-r}), 0.86 (t, J = 6.8 Hz, 3H, H_s).

^{13}C NMR (101 MHz, $CDCl_3$) δ 130.03 ($C_{J,K}$), 63.02 (C_B), 32.87 (C_C), 32.02 (C_Q), 29.87 ($C_{H,M}$), 29.54 (C_E), 29.73 – 29.28 ($C_{F,G,N,O,P}$), 27.30 ($C_{I,L}$), 25.87 (C_D), 22.79 (C_R), 14.20 (C_S).

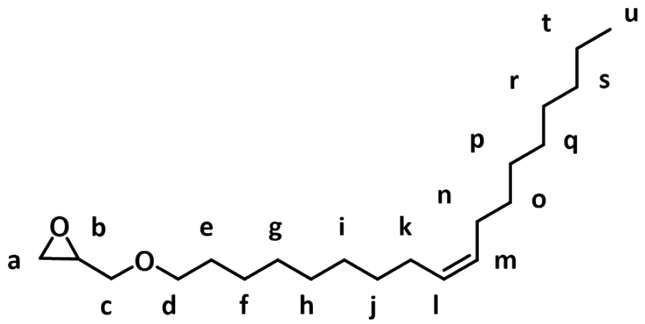
Synthesis of oleyl glycidyl ether from oleyl alcohol

The following procedure was adapted from Mouzin *et al*.[3]

A 500 mL three-necked round-bottom flask equipped with a mechanical stirrer, dropping funnel, and plug was charged with oleyl alcohol (21.87 g, 81.5 mmol, 1 eq.), tetra-*n*-butylammonium hydrogen sulfate (1.134 g, 3.34 mmol, 0.041 eq.), and 50 *w*.-% aqueous NaOH (60.6 mL). Toluene (29.27 mL) was introduced, and the biphasic mixture was vigorously stirred while being cooled in an ice/water bath. Epichlorohydrin (22.85 mL, 432 mmol, 5.3 eq.) was added dropwise *using* a dropping funnel. Upon complete addition, the cooling bath was removed, and the reaction mixture was allowed to react overnight. Subsequently, water (250 mL) was carefully added to the reaction mixture under ice cooling, followed by brief stirring to dissolve the precipitate. The phases were separated, and the aqueous phase was subjected to three extractions with 200 mL of petroleum ether each. The combined organic

phases were washed with brine until a neutral pH was reached and then dried using $MgSO_4$. Subsequent removal of the solvents and residual epichlorohydrin was achieved under high vacuum.

To purify the crude product and to eliminate the side product, 3-chloroallyl glycidyl ether, fractional distillation was performed using a Kugelrohr apparatus at 140 °C (pressure: $5 \cdot 10^{-3}$ mbar). The fraction obtained at 185–198 °C was collected and further purified by column chromatography using a gradient eluent ranging from 50/1 to 8/1 (V_{Cy}/V_{EtOAc}). The final yield of the pure product from the four columns was determined to be 18.62 g (57.5 mmol), corresponding to a 71% yield.



Yield: 71%

Purification by column chromatography, R_F=0.4, eluent 6/1 (V_{cy}/V_{EtOAc})

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.37 – 5.27 (m, 2H, $H_{l,m}$), 3.68 (dd, J = 11.5, 3.1 Hz, 1H, $H_{c'}$), 3.53 – 3.40 (m, 2H, H_d), 3.36 (dd, J = 11.5, 5.8 Hz, 1H, $H_{c''}$), 3.16 – 3.08 (m, 1H, H_b), 2.81 – 2.72 (m, 1H, $H_{a'}$), 2.62 – 2.54 (m, 1H, $H_{a''}$), 2.06 – 1.92 (m, 4H, $H_{k,n}$), 1.62 – 1.51 (m, 2H, H_e), 1.36 – 1.21 (m, 22H, $H_{f\text{-}j}$, $H_{o\text{-}t}$), 0.86 (t, J = 6.7 Hz, 3H, H_u).

^{13}C NMR (101 MHz, $CDCl_3$) δ 129.95 ($C_{L,M}$), 71.79 (C_D), 71.55 (C_C), 50.96 (C_B), 44.37 (C_A), 32.01 (C_S), 29.86 ($C_{J,O}$), 29.80 (C_E), 29.67 – 29.34 ($C_{G,H,I,P,Q,R}$), 27.29 ($C_{K,N}$), 26.18 (C_F), 22.78 (C_T), 14.19 (C_U).

Polymerization Procedures

Synthesis of mPEG-*b*-POlGE block copolymers

The following procedure outlines the synthesis of block copolymers using monomethyl poly(ethylene glycol) (mPEG) initiators with molecular weights of 2000 and 5000 g/mol. The specific example described here is the synthesis of $mPEG_{114}$-*b*-$POlGE_{9.9}$.

In a flame-dried Schlenk flask equipped with a rubber septum and a neodymium magnetic stirring bar, mPEG (5000 g/mol, 650 mg, 0.13 mmol, 1 eq.) and KO^{t}Bu (13.1 mg, 0.117 mmol, 0.9 eq.) were dissolved in 8 mL of benzene, along with dry [18]crown-6 (61.9 mg, 0.234 mmol, 1.8 eq., 2 eq. towards KO^{t}Bu). The mixture was then heated at 60 °C under reduced pressure for approximately one hour. Subsequently, the solvent was removed under high vacuum at room temperature. When most of the solvent had evaporated, the temperature was maintained at 60 °C overnight, forming the dried initiator salt.

The monomer (OlGE) was dried by azeotropic distillation using benzene. OlGE was mixed with 8 mL of benzene in a flame-dried Schlenk flask. The mixture was subsequently frozen with liquid nitrogen, and the solvent was removed under reduced pressure at room temperature overnight. The monomer was then heated to 60 °C under a high vacuum for 1 h to remove any residual benzene.

Next, OlGE (0.60 mL, 506 mg, 12 eq.) was added to the initiator salt at 80 °C and stirred overnight to initiate polymerization in bulk. The reaction was terminated by adding a mixture of 1 M hydrochloric acid (0.117 mmol, 0.9 eq., 1 eq. to KO^{t}Bu), and 1 mL of MeOH, followed by stirring for a few minutes. The polymer was then suspended in *n*-pentane at room temperature and frozen overnight. The resulting mixture was centrifuged, decanted, and suspended in fresh *n*-pentane, and the procedure was repeated. Subsequently, the polymer was dialyzed against MeOH using a dialysis tube with a molecular weight cut-off (MWCO) of 2000 g/mol to remove any potentially unreacted monomer as well as crown ether. The dialysis medium was exchanged after approximately 3 and 18 h. The workup procedures for the different polymers were varied and are summarized in Table S1. Polymers that were

dissolved in solvents at or above room temperature did not precipitate sufficiently and needed to be deep-frozen.

Table S1: mPEG-*b*-POlGE block copolymers and their respective workup.

Polymer	Precipitation medium	MWCO dialysis tube
$mPEG_{45}$-*b*-$POlGE_{2.4}$	MeOH (RT), then freezer	1000 g/mol
$mPEG_{45}$-*b*-$POlGE_{5.0}$	MeOH (50 °C), then freezer	1000 g/mol
$mPEG_{45}$-*b*-$POlGE_{7.5}$	MeOH (50 °C), then freezer	1000 g/mol
$mPEG_{45}$-*b*-$POlGE_{11.3}$	*Dialysis against THF	1000 g/mol
$mPEG_{114}$-*b*-$POlGE_{2.9}$	*n*-Pentane (-18 °C)	2000 g/mol
$mPEG_{114}$-*b*-$POlGE_{5.8}$	*n*-Pentane (-18 °C)	2000 g/mol
$mPEG_{114}$-*b*-$POlGE_{7.3}$	*n*-Pentane (RT), then freezer	2000 g/mol
$mPEG_{114}$-*b*-$POlGE_{9.9}$	*n*-Pentane (RT), then freezer	2000 g/mol

After dialysis, the solvent was removed, and the final product was dried under high vacuum at 60 °C overnight, yielding 508 mg, which corresponded to a yield of 44%.

Synthesis of statistical P(EG-*co*-OlGE) copolymers

Please note that the procedure relies on the use of ethylene oxide, a toxic and flammable gas which should be treated with caution. We would like to note that the notation "*co*" refers to any kind of copolymer. In principle, the abbreviation "*stat*" would be more precise, however, it is rarely found in the literature. The synthesis of statistical copolymers using 2-(benzyloxy)ethanol as an initiator, with P(EG_{123}-*co*-$OlGE_7$) as a specific example, was conducted as follows.

In a flame-dried custom-made anionic flask equipped with a Teflon stopcock, rubber septum, and magnetic stirrer, $CsOH{\cdot}H_2O$ (24.8 mg, 0.148 mmol, 0.9 eq.) and 2-(benzyloxy)ethanol (25 mg, 0.164 mmol, 1 eq.) were dissolved in 8 mL of benzene. The mixture was heated at 60 °C under static

vacuum for 1 h. Subsequently, the solvent was removed under vacuum and the residue was further heated at 60 °C overnight to obtain the dried initiator salt.

The monomer (OlGE) was dried by azeotropic distillation using benzene. OlGE was mixed with 8 mL of benzene in a flame-dried Schlenk flask. The mixture was then frozen with liquid nitrogen, and the solvent was removed under reduced pressure at room temperature overnight. The monomer was further heated to 60 °C under high vacuum for 1 h to remove any residual benzene.

Next, the initiator salt was dissolved in 0.83 mL of DMSO (dried over molecular sieves) and dry THF (4.17 mL) was condensed into a glass ampule using an ethanol/liquid nitrogen cooling bath. The condensed THF was then cryo-transferred to the anionic flask. The solvents were then mixed at room temperature and frozen in the cooling bath. Following this, OlGE (320 mg, 0.38 mL, 0.986 mmol, 6 eq.) was then added using a syringe. Ethylene oxide (EO) (0.83 mL at 80 °C, 18.73 mmol, 114 eq.) was condensed into a glass ampule and cryo-transferred to the anionic flask with the cooling bath. The resulting mixture was stirred at 40 °C for at least 72 h to ensure complete EO consumption during copolymerization.

After polymerization, the reaction was terminated by adding a mixture of 1 M hydrochloric acid (0.148 mmol, 0.9 eq., 1 eq. to $CsOH{\cdot}H_2O$) and 1 mL of MeOH. The solvents were roughly removed by a strong nitrogen flow through the anionic flask. The raw product was then dissolved in DCM and extracted three times with water to remove DMSO. The resulting polymer was dialyzed against MeOH using a membrane with a molecular weight cut-off (MWCO) of 1000 g/mol, with the dialysis medium being exchanged after 3 and 18 h. The solvents were removed, and the polymer was dried at 60 °C under high vacuum, resulting in a yield of 883 mg, which corresponds to 77% yield.

Synthesis of POlGE homopolymers

The following procedure describes the synthesis of POlGE homopolymers using 2-(benzyloxy)ethanol as the initiator and $POlGE_{25}$ as an illustrative example.

In a flame-dried Schlenk flask equipped with a rubber septum and a neodymium magnetic stirring bar, 2-(benzyloxy)ethanol (15 mg, 98.6 µmol, 1 eq.) and KO^{t}Bu (10 mg, 88.7 µmol, 0.9 eq.) together with [18]crown-6 (46.9 mg, 0.177 mmol, 1.8 eq., 2 eq. to KO^{t}Bu) were dissolved in benzene (8 mL). The mixture was heated at 60 °C under static vacuum. After one hour, the solvents were removed *in vacuo* to yield the dried initiator salt. Azeotropic distillation with benzene was used to dry the OlGE monomer. First, a Schlenk flask equipped with a magnetic stirrer was heated in flame. Subsequently, more OlGE than required for the batch was mixed with benzene (8 mL). The benzene was subsequently removed under vacuum overnight, resulting in dried OlGE. OlGE (0.94 mL, 800 mg, 2.46 mmol) was transferred to the initiator salt at 80 °C under an Ar counterflow using a syringe. The polymerization was allowed to proceed for 18 h. Subsequently, the polymerization was terminated using a mixture of 1 M hydrochloric acid (88.7 µmol, 1 eq. to KO^{t}Bu) and 1 mL MeOH. The mixture was dissolved in a small amount of DCM and precipitated using ice-cold MeOH. After centrifugation for at least 45 min, the solvent was decanted, and the procedure was repeated twice. Heating of the polymer at 60 °C yielded 650 mg, corresponding to 80% yield.

***In situ* ^{1}H NMR kinetic investigation of the statistical copolymerization of EO and OlGE**

A *Norell S-500-VT-7* sealable NMR tube with a Teflon stopcock was used to determine the reactivity ratios of EO and OlGE. The setup was similar to that described by Frey *et al*.[4] Preparation of the initiator salt (cesium 2-(benzyloxy)ethanolate) was carried out in a five-fold batch, as described on page 8. The initiator salt was dissolved in the respective amount of DMSO-d_6, yielding an initiator stock solution. EO was condensed into the oven-dried NMR tube under static vacuum employing an acetone/nitrogen cooling bath. Next, THF-d_8 (which had been dried over CaH_2), dry OlGE, and one-fifth of the initiator stock solution were added while cooling under Ar counterflow. The mixture underwent three freeze-pump-thaw cycles to remove any remaining gas and was then cooled with liquid nitrogen before being inserted into the preheated NMR spectrometer at 40 °C. Sample spinning was turned off, and a spectrum was recorded before measuring the receiver gain. Online kinetic was conducted at 40 °C for

55 hours, with one scan every two minutes. Following the kinetic study, the copolymer underwent SEC analysis.

The distinctive chemical shift of the OlGE and EO epoxide functionality was observed, enabling to track the consumption of each respective monomer. The software NIREVAL, created by Frey *et al*.,[5] was utilized to analyze the normalized monomer consumption.

Post-polymerization procedures

Thiol-Ene Click

To modify the polymer $mPEG_{114}$-*b*-$POlGE_{2.9}$, the following steps were carried out. First, 50 mg (8.33 µmol, 1 eq.) of the polymer was dissolved in DCM (0.3 mL) along with the photoinitiator 2,2-dimethoxy-2-phenylacetophenone (DMPA, 12.8 mg, 50 µmol, 6 eq.) in a 10 mL Schlenk tube with a magnetic stirring bar and rubber septum. Then, thioglycol (78.1 mg, 1 mmol, 120 eq., 40 eq. per double bond) was added to the mixture, and an additional 0.3 mL DCM was flushed into the tube. The mixture was subjected to three freeze-pump-thaw cycles and was then irradiated overnight under continuous stirring using a UV lamp with a wavelength of 254 nm at a 5 cm distance. Next, the mixture was diluted with DCM (10 mL) and extracted three times against water (15 mL) to remove any unreacted thioglycol. The organic phase was dialyzed (MWCO 2000 g/mol) against MeOH (1 L, solvent changed three times). After solvent evaporation, the material was dried under high vacuum at 60 °C, the modified polymer (42 mg) was obtained in 84% yield.

Hydrogenation

For post-polymerization hydrogenation, the *in situ*-formed diimide was utilized. It was generated by the acidic decomposition of potassium azodicarboxylate (PADA):

Synthesis of potassium azodicarboxylate (PADA)

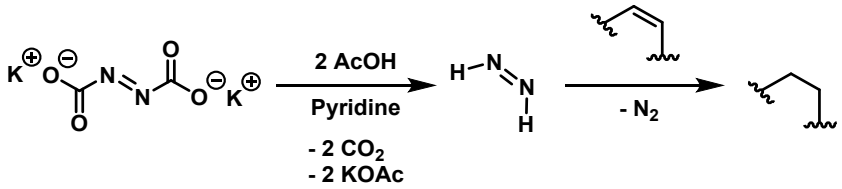
The described procedure was inspired by Ma and Groves.[6]

To synthesize PADA, 30 mL of a 40% aqueous potassium hydroxide solution was added to a 50 mL round-bottom flask with a magnetic stirrer. The flask was then placed into a water bath at 6 °C. Azodicarboxylate (4.84 g, 41.7 mmol) was added slowly over 2 hours. Afterward, the precipitate was filtered using a glass frit with filter paper and washed 20 times with ice-cold methanol. Finally, the product was dried in a desiccator for 1.5 days under vacuum, resulting in an intense yellow powder with a yield of 7.18 g, 37.0 mmol, or 89%.

Hydrogenation as post-polymerization modification

The utilization of PADA to generate diimide is a distinctive approach. In our study, we adjusted the synthesis methods previously reported by Groves and Ma,[6] as well as Snyder and Hamersma.[7] We also applied the method towards a similar system.[8]

Please note, that the *in situ* diimide generation may produce toxic hydrazine as a byproduct.



Scheme S1: Diimide generation of PADA by acidic decomposition, followed by polymer hydrogenation. Coupling products include gaseous carbon dioxide, nitrogen, and water-soluble potassium acetate.

Hydrogenation was applied for the homopolymer $POlGE_{25}$ aiming at different degrees of hydrogenation. The procedure described here for the synthesis of $POlGE_{25}$ (H95%) (degree of hydrogenation 95%) was as follows: $POlGE_{25}$ (50 mg, 6.02 µmol, 1 eq.) was transferred into a flame-dried Schlenk tube equipped with a magnetic stirrer and a rubber septum using toluene. The solvent was removed *in vacuo*, resulting in the azeotropically dried substrate. The polymer was dissolved in 2.4 mL of pyridine, which had been previously dried over molecular sieves. To this solution, PADA (439 mg, 2.26 mmol, 375 eq., 15 eq. to the double bonds) was added. Additionally, 0.27 mL of glacial acetic acid, previously dried over P_4O_{10}, was mixed with 0.6 mL of dry pyridine. This acetic acid-pyridine mixture was then slowly added to the stirred polymer solution over 14 hours using a syringe pump, with the dead volume of the tube considered for precise proportion. After complete addition, the mixture was further stirred for at least 2 hours until the colorless precipitate dissolved in water. The aqueous phase was then subjected to two extractions with chloroform (10 mL each), while the organic phase underwent three extractions with water (10 mL each) to remove any remaining salts. Next, the solvent was removed, and the resulting hydrogenated polymer was dried under high vacuum at 60 °C overnight to obtain the final product (47 mg) in 94% yield. To reach a hydrogenation level of 76% in

$POlGE_{25}$ (H76%), three equivalents of PADA were required per double bond. On the other hand, to achieve a hydrogenation level of 53% in $POlGE_{25}$ (H53%), 1.25 equivalents of PADA were required per double bond.

NMR Spectra of OlGE

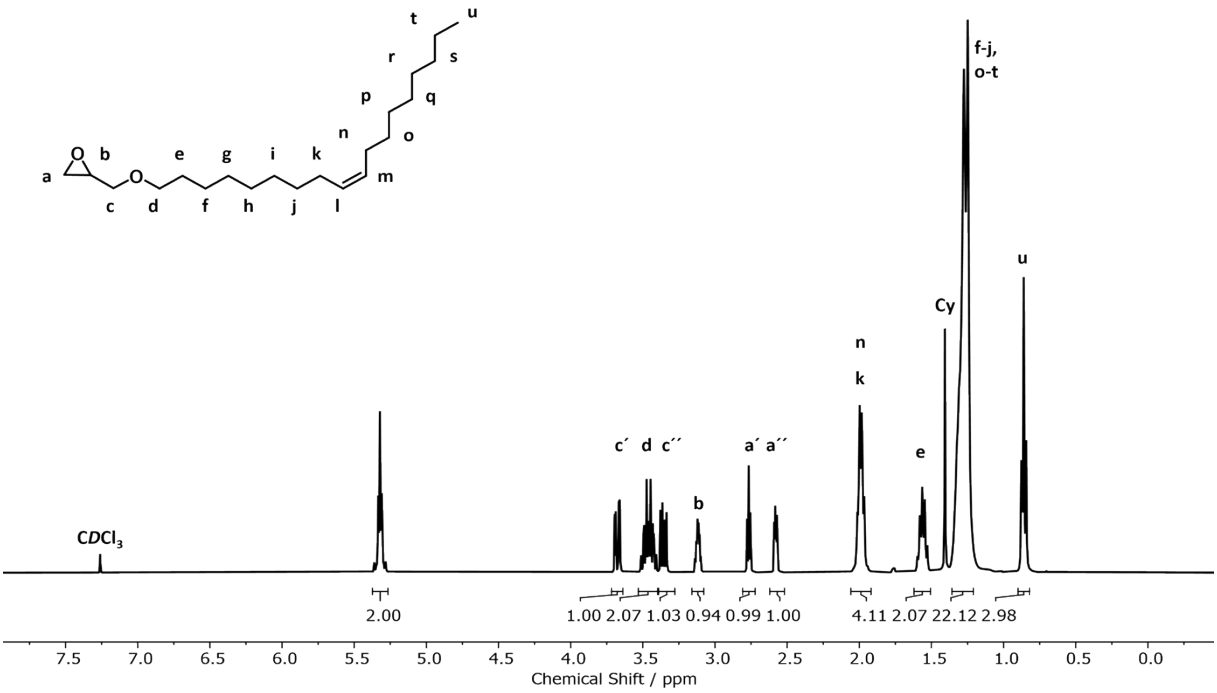


Figure S1: ^{1}H NMR spectrum of oleyl glycidyl ether (OlGE) ($CDCl_3$, 400 MHz).

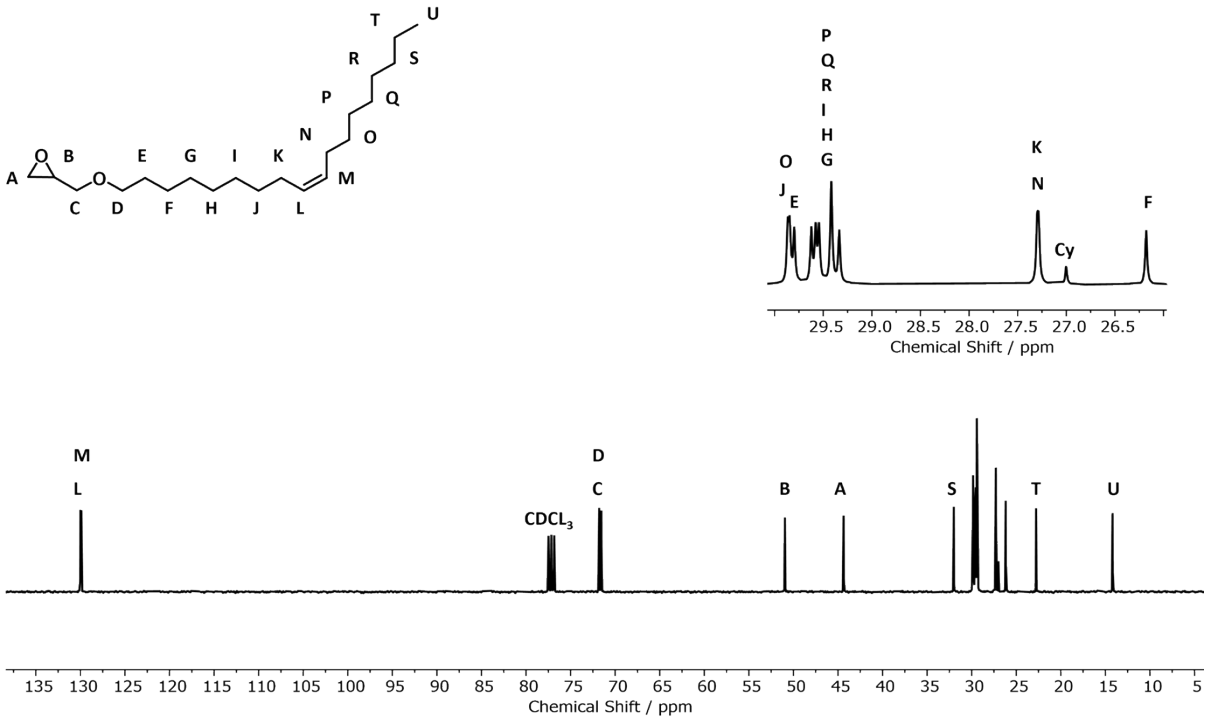


Figure S2: ^{13}C NMR spectrum of oleyl glycidyl ether (OlGE) (101 MHz, $CDCl_3$).

Characterization of Block copolymers of OlGE and EO

OlGE repeating units could not be calculated by integration of the initiator methoxy group due to the shift of the backbone into the highfield after copolymerization. Instead, the following equation was used to determine the OlGE repeating units (*n*(OlGE)) from the integral of the mPEG precursor and the integral of the synthesized polymer.

$$n(OlGE) = \frac{I(mPEG)}{I(Backbone) - 7} \quad \text{(S2)}$$

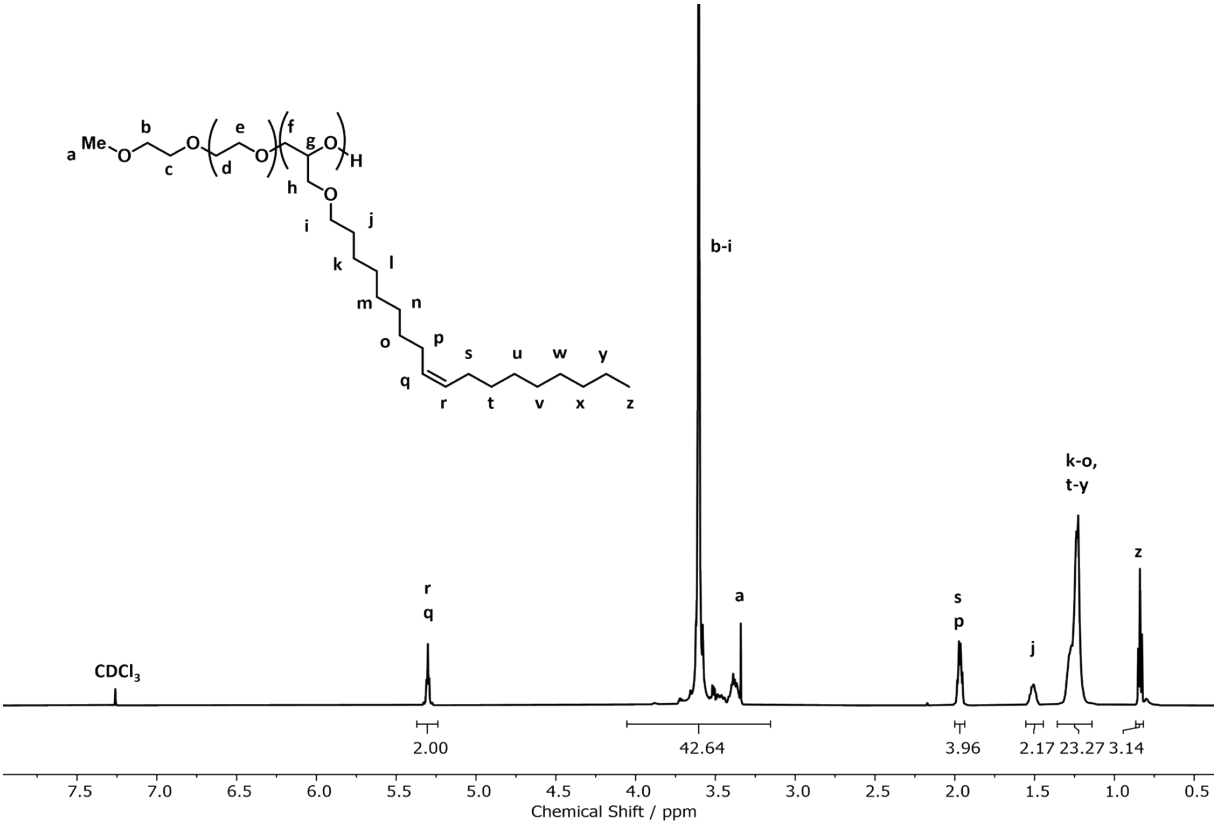


Figure S3: ^{1}H NMR spectrum of mPEG-*b*-POlGE (600 MHz, $CDCl_3$, 21 °C).

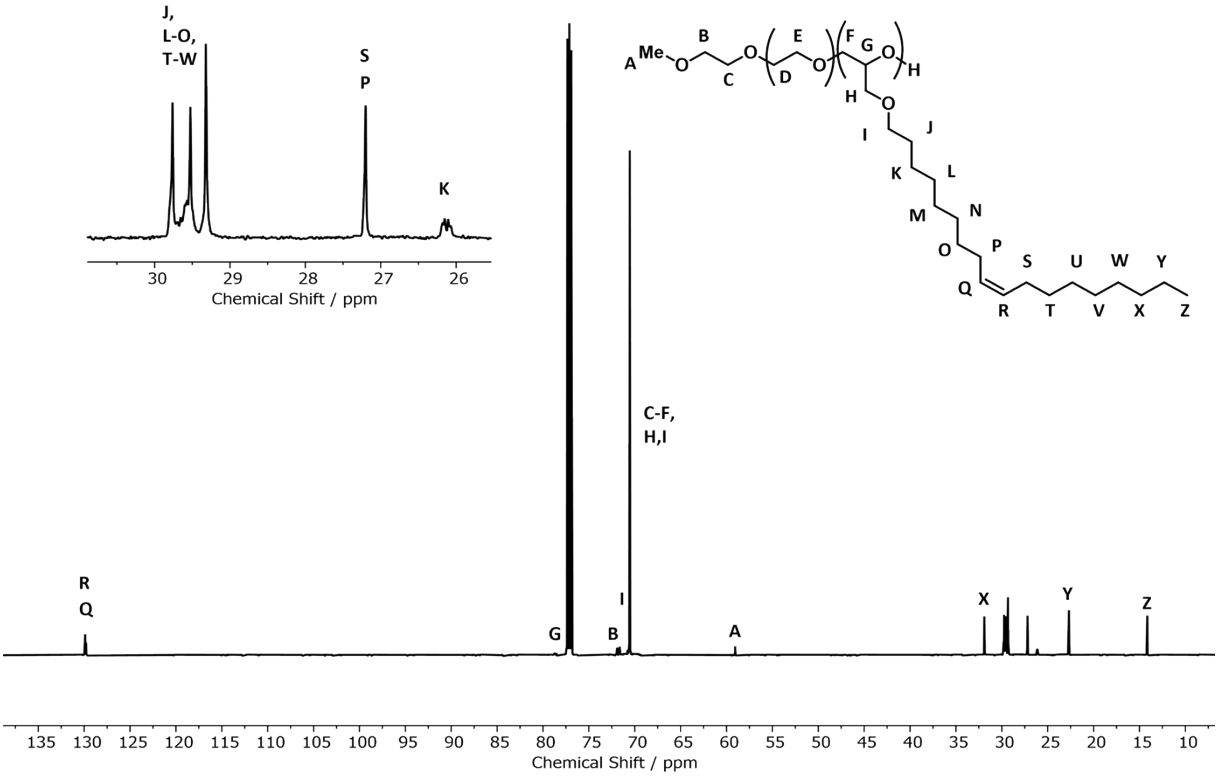


Figure S4: ^{13}C NMR spectrum of mPEG-*b*-POlGE (151 MHz, $CDCl_3$, 21 °C).

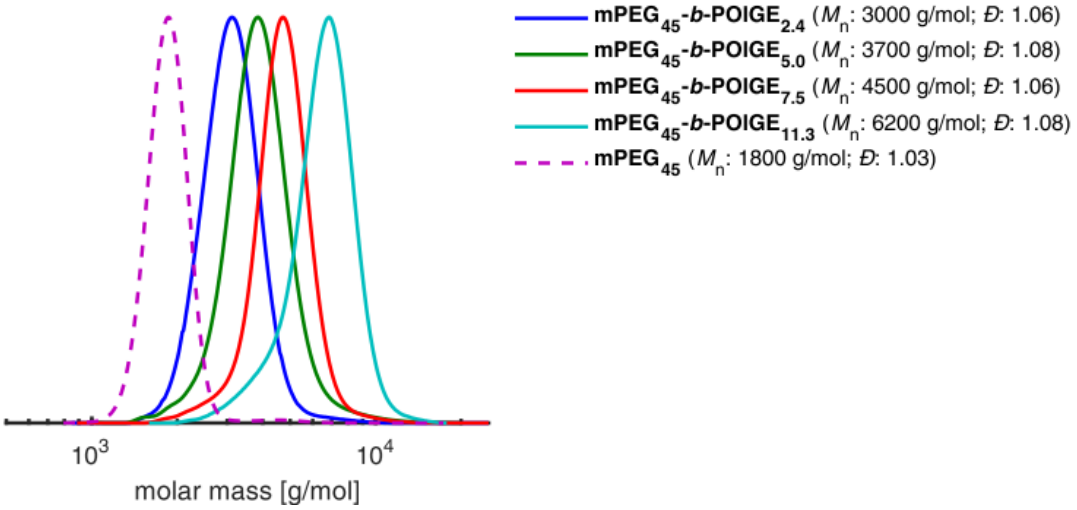


Figure S5: SEC traces of $mPEG_{45}$-*b*-POlGE (RI detector, eluent: THF, PEG calibration).

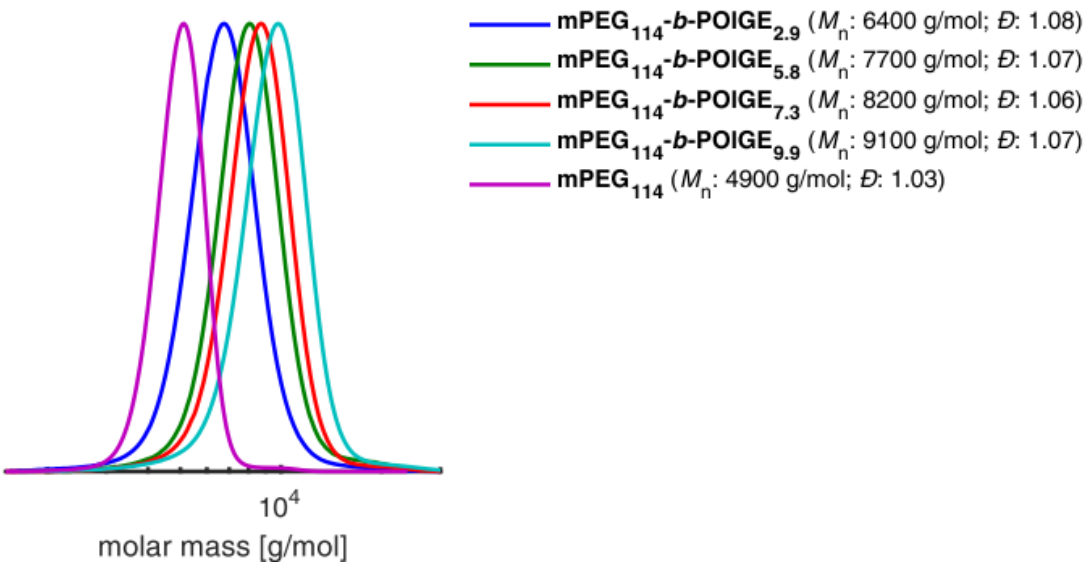


Figure S6: SEC traces of mPEG$_{114}$-*b*-POlGE (RI detector, eluent: THF, PEG calibration).

Characterization of statistical copolymers of OlGE and EO

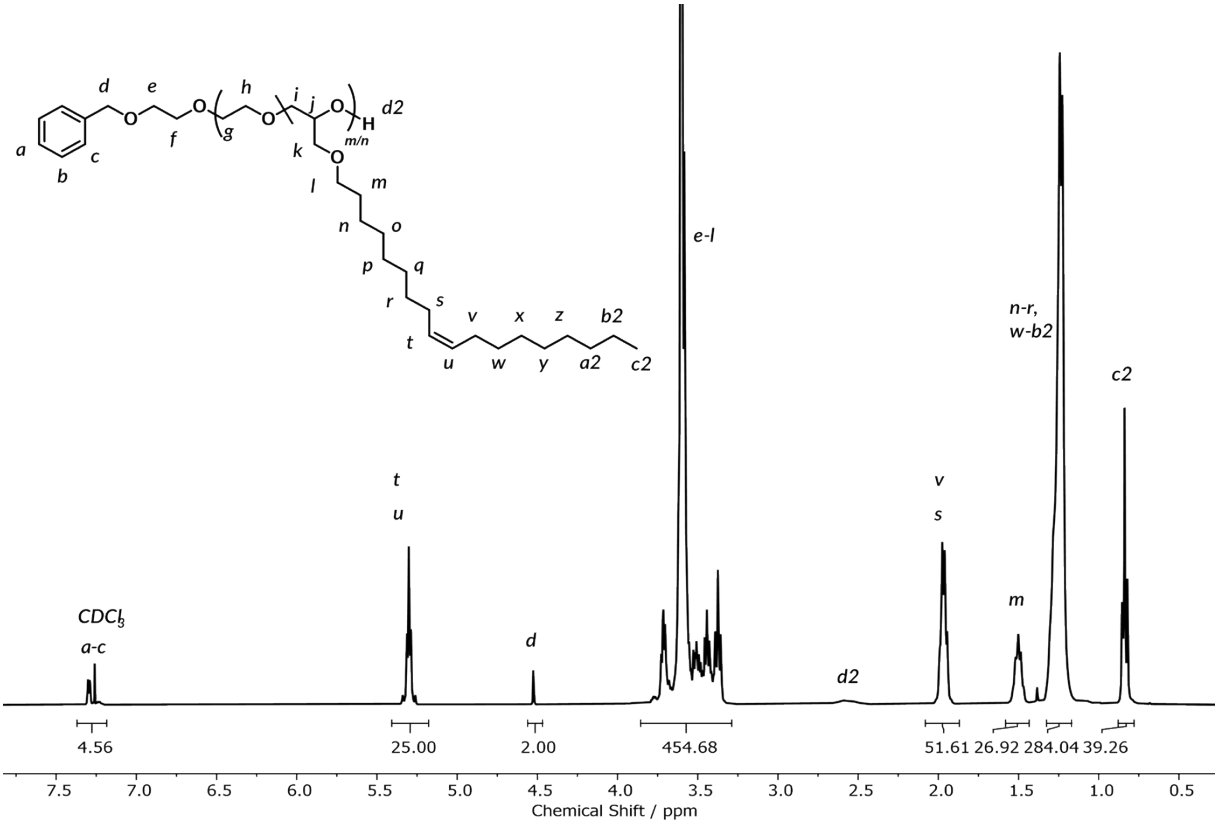


Figure S7: ^{1}H NMR of a statistical P(EG-*co*-OlGE) copolymer (400 MHz, $CDCl_3$).

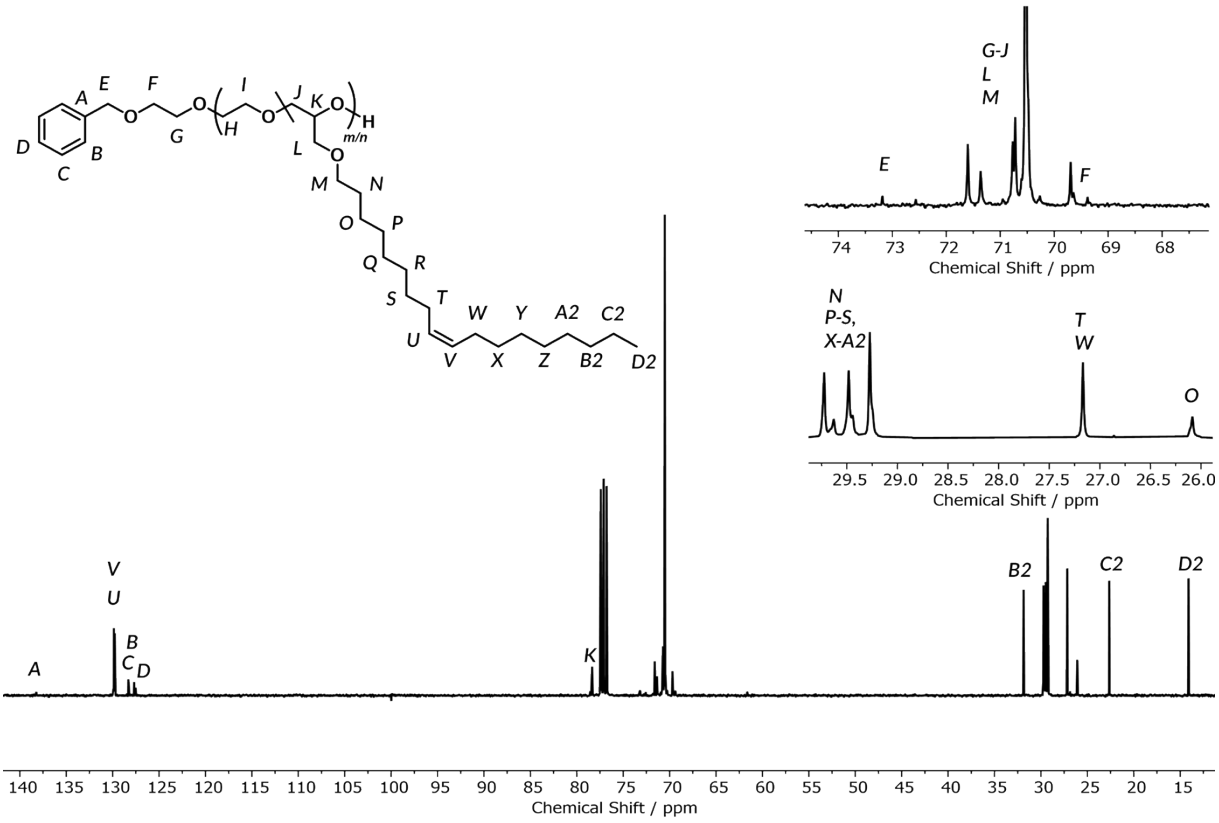


Figure S8: ^{13}C NMR of a statistical P(EG-*co*-OlGE) copolymer (101 MHz, $CDCl_3$).

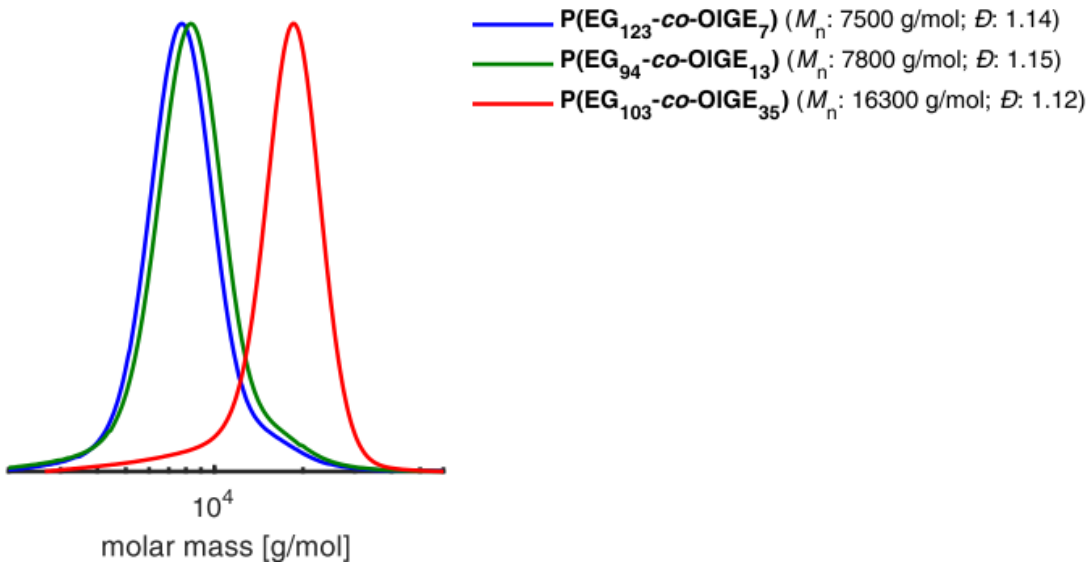


Figure S9: SEC traces of statistical P(EG-*co*-OlGE) copolymers (RI detector, eluent: THF, PEG calibration).

Characterization of Homopolymers of OlGE

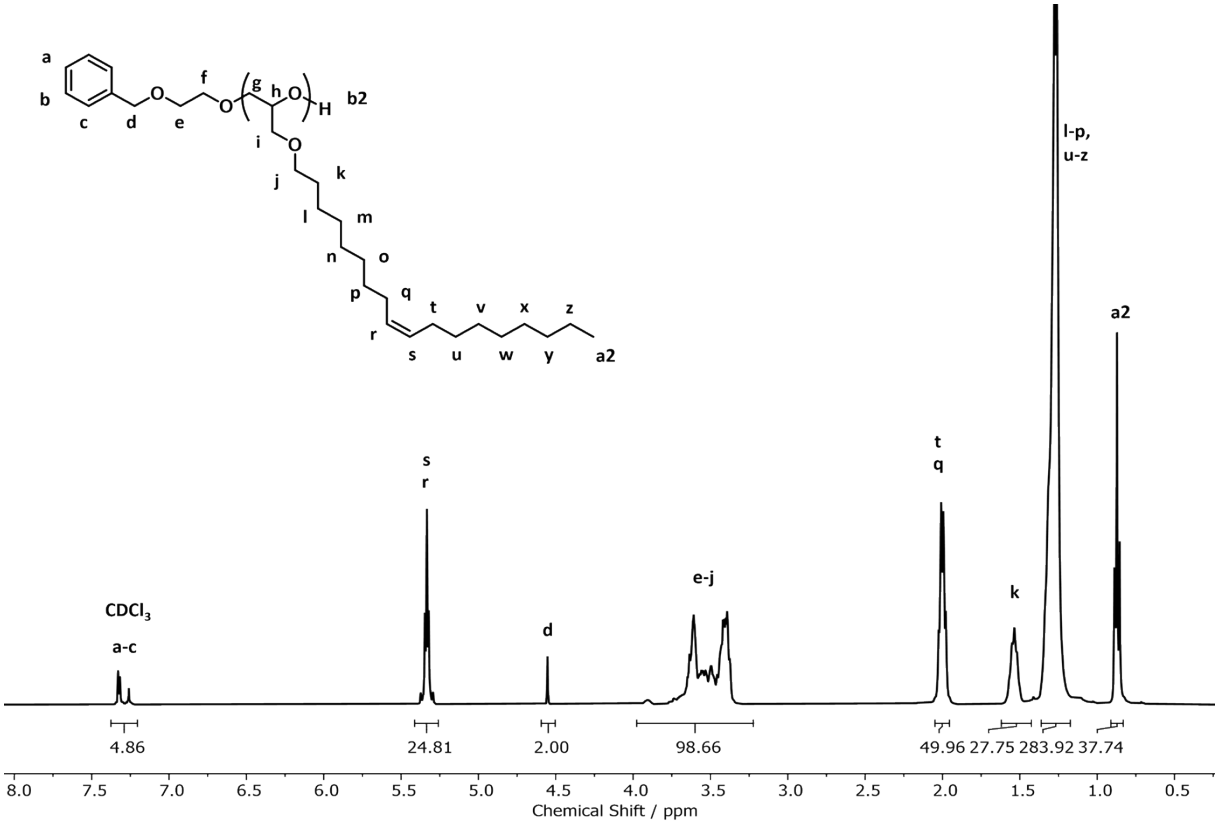


Figure S10: ^{1}H NMR spectrum of POlGE homopolymer (400 MHz, $CDCl_3$).

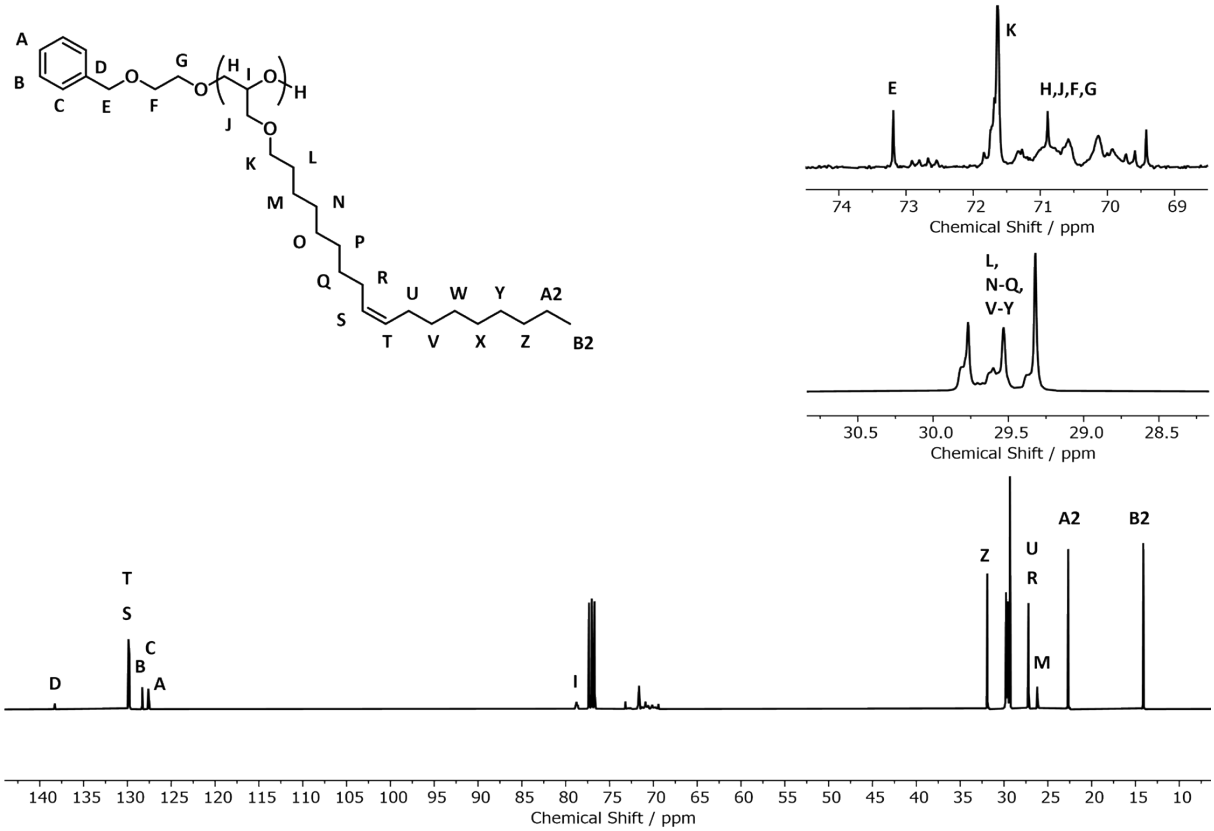


Figure S11: ^{13}C NMR spectrum of a POlGE homopolymer sample (101 MHz, $CDCl_3$).

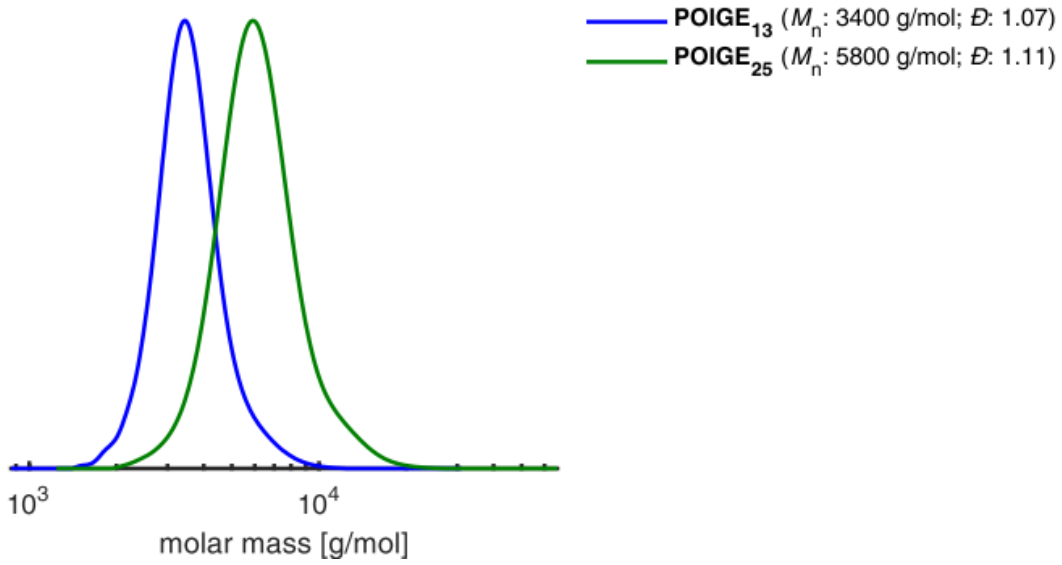


Figure S12: SEC traces of POlGE homopolymers (RI detector, eluent: THF, PEG calibration).

Thermal Characterizations of Polymers

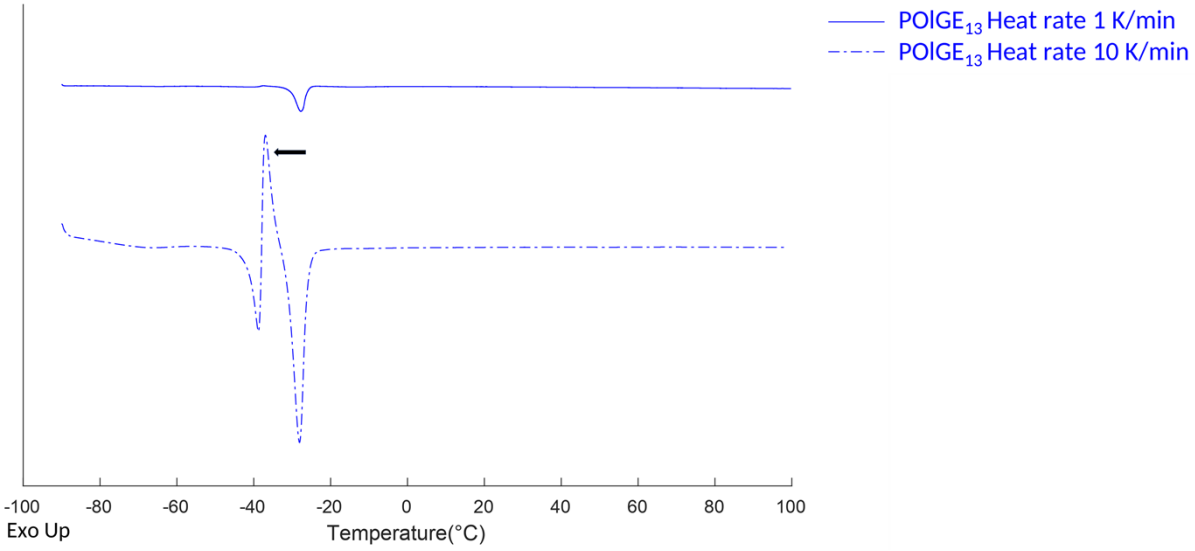


Figure S13: DSC thermograms of POlGE homopolymer measured at different heating and cooling rates; second heating curve. Black arrow marks a strong recrystallization peak at a heating rate of 10 K/min.

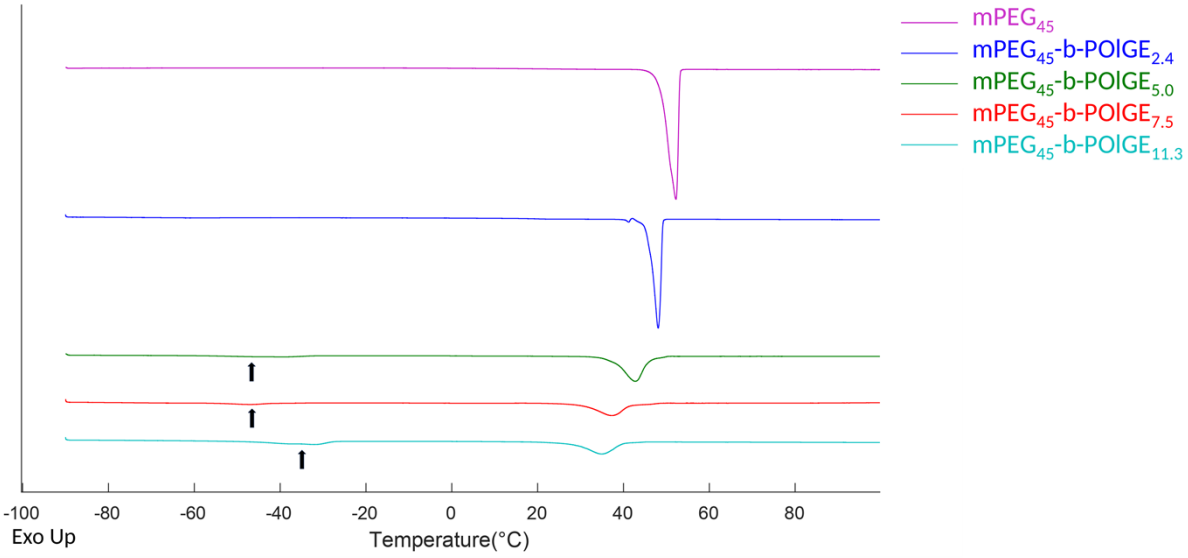


Figure S14: DSC thermograms of $mPEG_{45}$-based OlGE block copolymers and the precursor. Second heating curve, 1 K/min. Melting areas, which are only visible in strong zoom, are marked by black arrows.

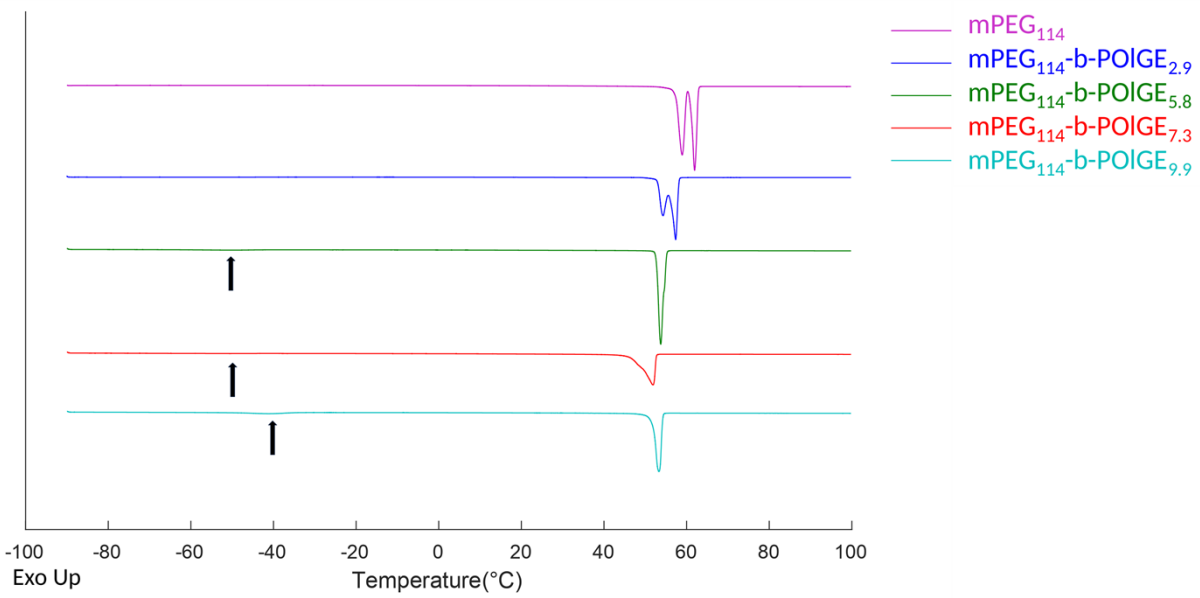


Figure S15: DSC thermograms of $mPEG_{114}$-based OlGE block copolymers and the precursor. Second heating curve, 1 K/min. Melting areas that are only visible in strong zoom are marked by black arrows.

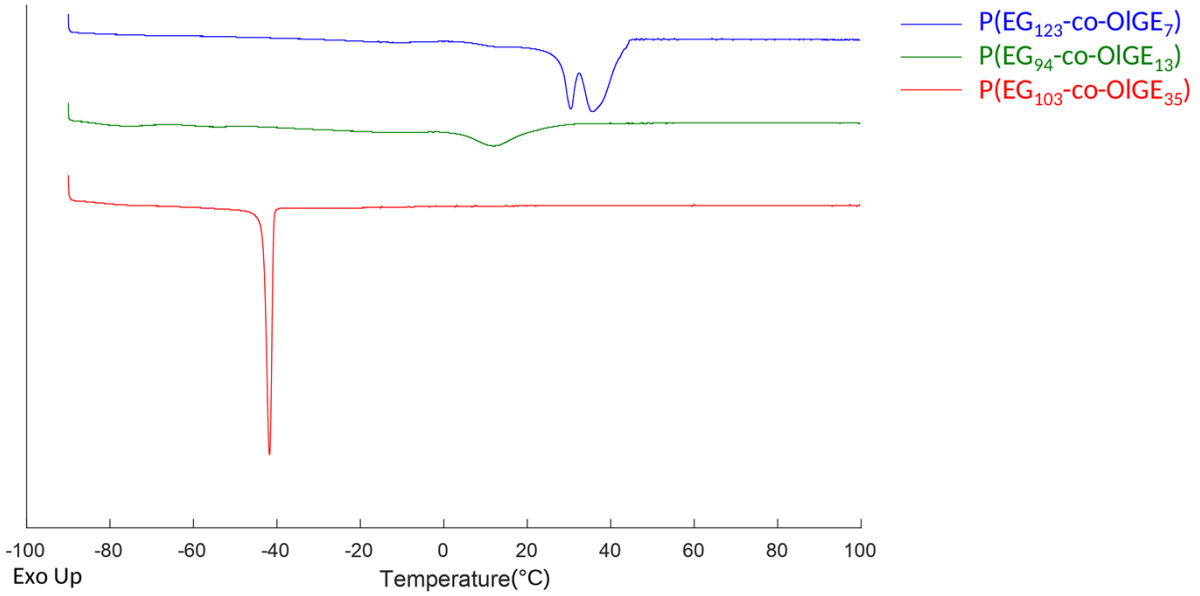


Figure S16: DSC thermograms of statistical EO/OlGE copolymers. Second heating curve, 1 K/min.

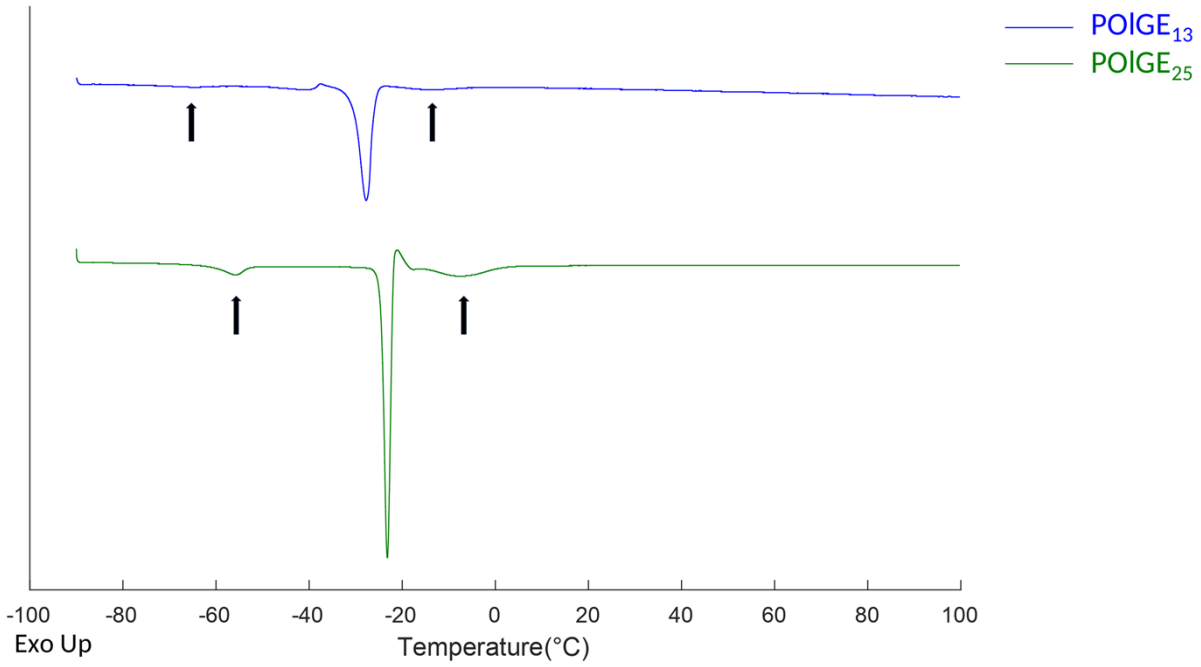


Figure S17: DSC thermograms of POlGE homopolymers. Second heating curve, 1 K/min. Melting areas that are only visible in strong zoom are marked by black arrows.

CMC determination by fluorescence spectroscopy

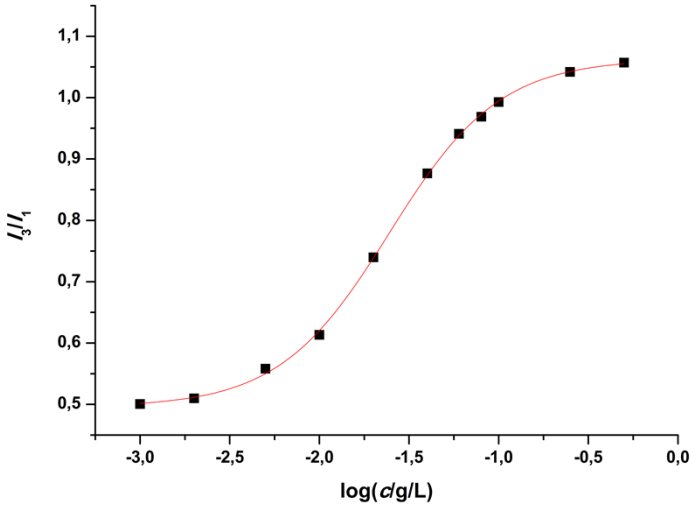


Figure S18: CMC determination of P(EG_{123}-*co*-$OIGE_7$) by fluorescence spectroscopy with pyrene as a probe. Black squares: data points, red line: fitting curve.

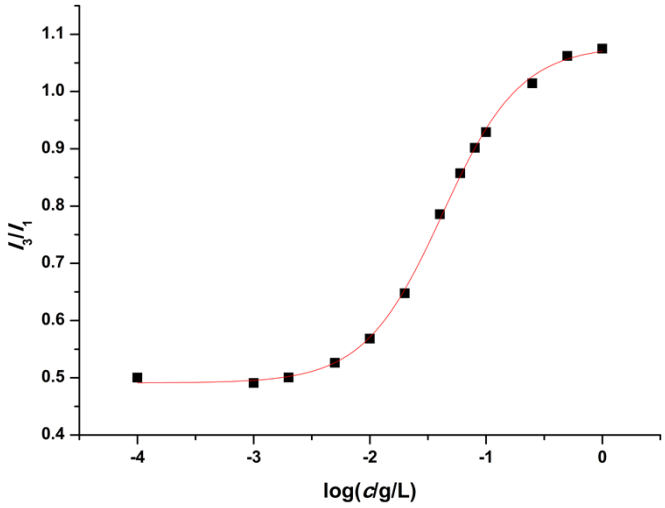


Figure S19: CMC determination of mPEG_{45}-*b*-$POIGE_{2.4}$ by fluorescence spectroscopy with pyrene as a probe. Black squares: data points, red line: fitting curve.

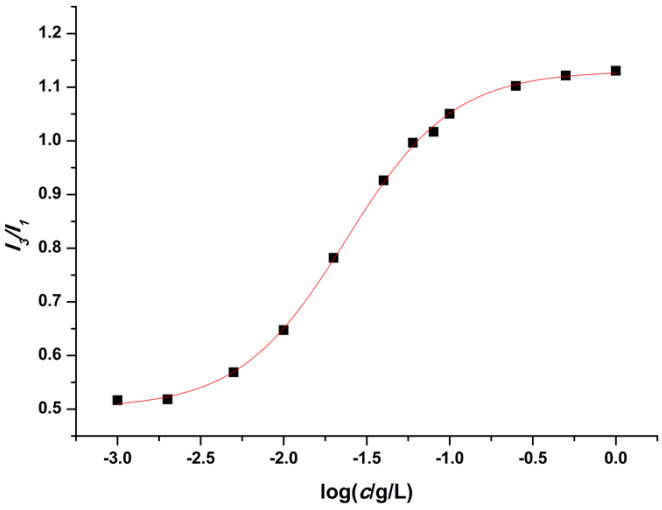


Figure S20: CMC determination of mPEG$_{45}$-*b*-POlGE$_{5.0}$ by fluorescence spectroscopy with pyrene as a probe. Black squares: data points, red line: fitting curve.

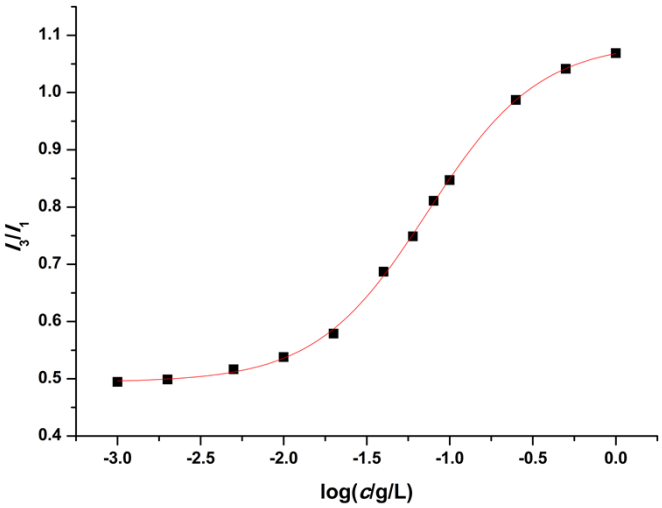


Figure S21: CMC determination of mPEG$_{114}$-*b*-POlGE$_{2.9}$ by fluorescence spectroscopy with pyrene as a probe. Black squares: data points, red line: fitting curve.

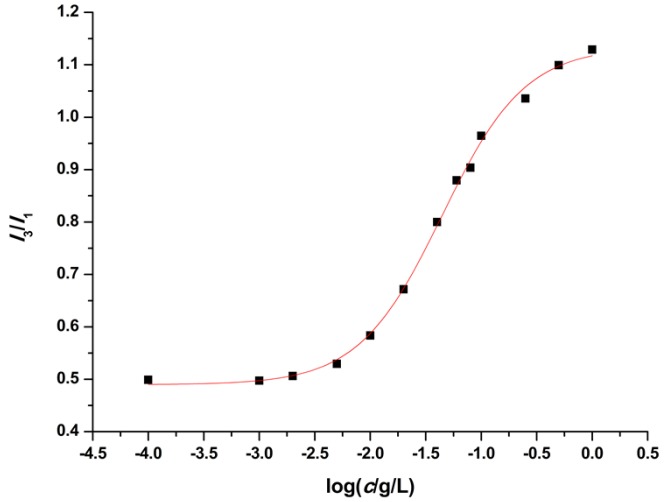


Figure S22: CMC determination of mPEG$_{114}$-*b*-POlGE$_{5.8}$ by fluorescence spectroscopy with pyrene as a probe. Black squares: data points, red line: fitting curve.

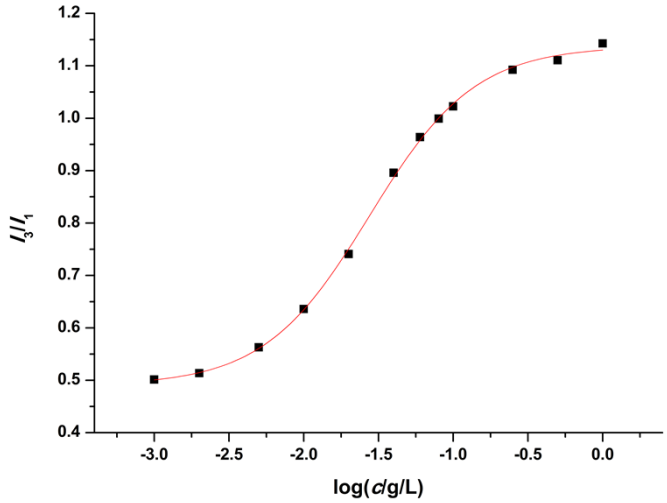


Figure S23: CMC determination of mPEG$_{114}$-*b*-POlGE$_{7.3}$ by fluorescence spectroscopy with pyrene as a probe. Black squares: data points, red line: fitting curve.

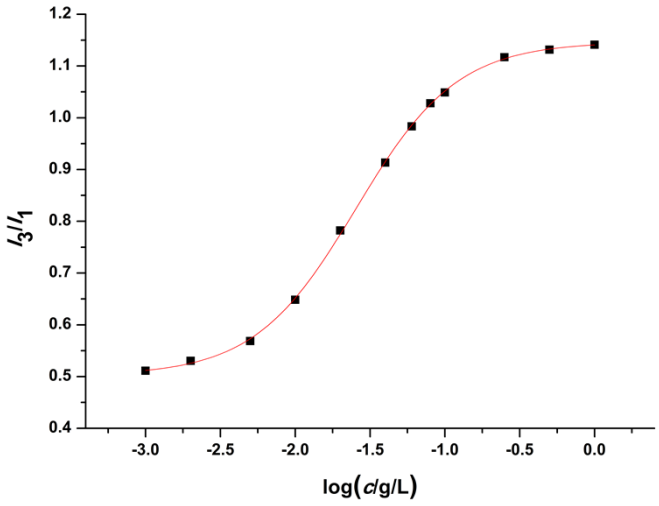


Figure S24: CMC determination of mPEG$_{114}$-*b*-POlGE$_{9.9}$ by fluorescence spectroscopy with pyrene as a probe. Black squares: data points, red line: fitting curve.

Transmission Electron Microscopy

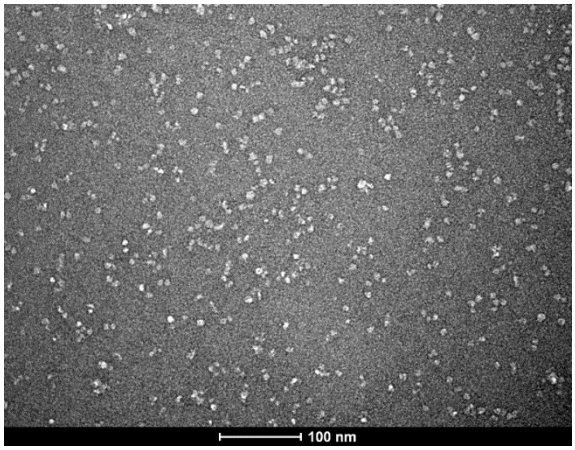
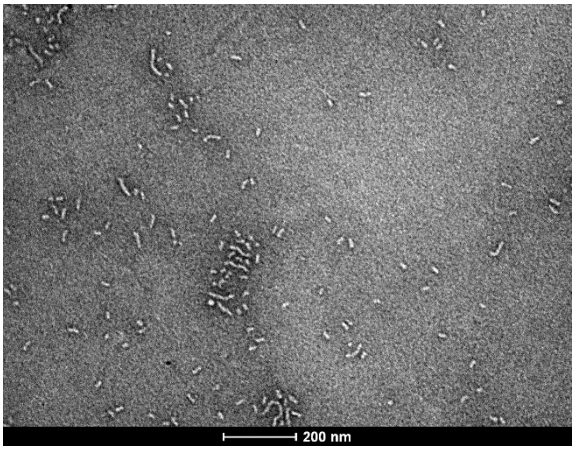


Figure S25: TEM micrograph of statistical P(EG_{123}-*co*-$OlGE_7$) copolymer in aqueous solution (0.1 g/L). Samples were treated with 2% uranyl acetate solution as negative stain.



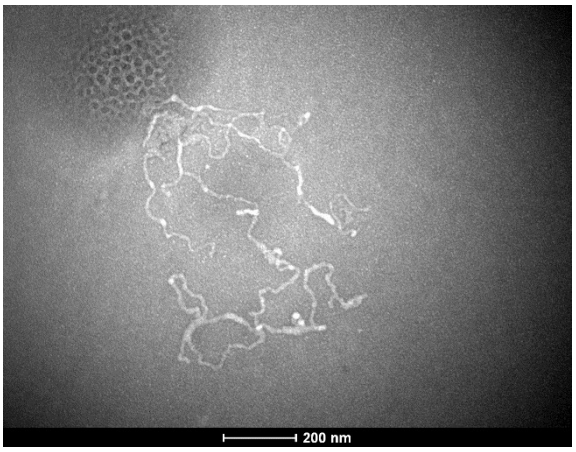
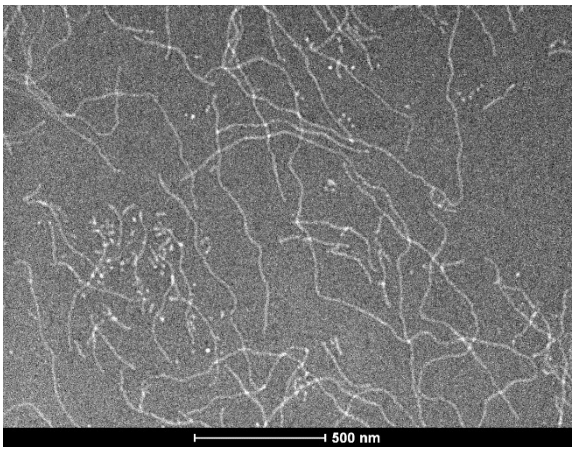


Figure S26: TEM micrograph of mPEG_{45}-*b*-$POlGE_n$ block copolymers in aqueous solution (0.1 g/L). Left: n=2.4, right: n=5.0. The circular structure in the upper left corner is caused by irradiation damage. Samples were treated with 2% uranyl acetate solution as negative stain.


100 nm


500 nm

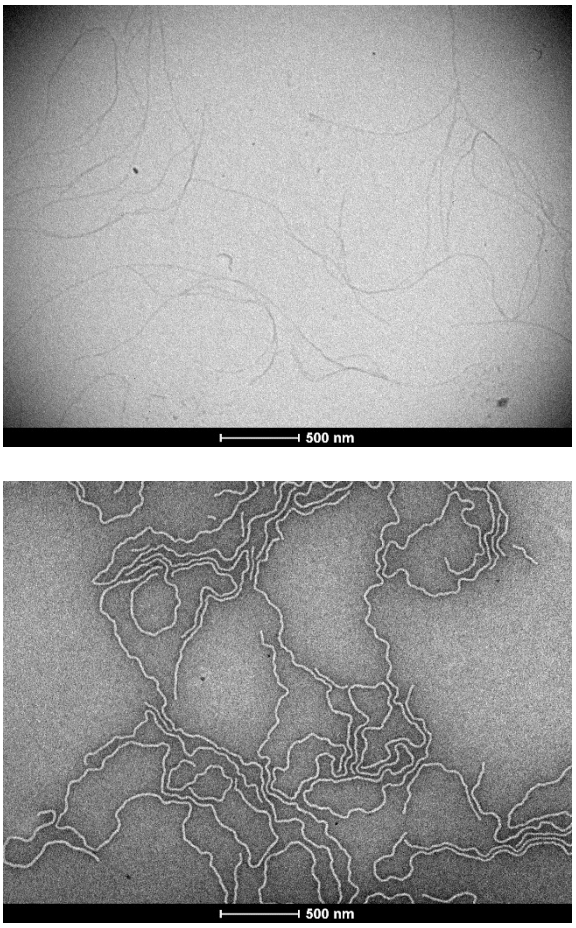


Figure S27: TEM micrograph of $mPEG_{114}$-*b*-$POlGE_n$ block copolymers in aqueous solution (0.1 g/L). Top left: *n*=2.9, top right: *n*=5.8. Bottom left: *n*=7.3, bottom right: *n*=9.9. Samples were treated with 2% uranyl acetate solution as negative stain.

Dynamic Light Scattering

Cylindrical quartz glass cuvettes were thoroughly cleaned with hot acetone before usage to ensure they were free of any dust particles. Temperature control was maintained using a *Huber Pilot One* thermostat manufactured by *Peter Huber Kältemaschinenbau AG*. The measurements were conducted at a temperature of 25 °C, with a polymer concentration of 0.3 g/L. To eliminate any dust contaminants from the polymer solution, the solutions were filtered through a *Millex*-HV filter (0.45 µm, 13 mm). The filtering process was carried out within a dust-free laminar flow box. The measurements were executed across an angular range from 30° to 150° in 10° increments. The laser was from Thorlabs and had a wavelength of 632.8 nm. The respective scattering vector q can be defined using the following equation, considering the refractive index of water n, the scattering angle θ and the wavelength λ:

$$q = \frac{4\pi n}{\lambda} sin(\theta/2) \tag{S3}$$

The amplitude autocorrelation functions $g^{(1)}(q,\tau)$ were fitted using the following biexponential function:

$$g^{(1)}(q,\tau) = A + B \cdot exp\left(-\frac{\tau}{\tau_{R,1}}\right) + C \cdot exp\left(-\frac{\tau}{\tau_{R,2}}\right) \tag{S4}$$

With time τ, baseline A, amplitudes B and C, as well as the characteristic relaxation times of the respective modes τ_R. The diffusion coefficient of each measured angle is received from the relation $D=(\tau_R \cdot q^2)^{-1}$. Graphing D in relation to q^2 yielded z-average D from the coordinate section. Applying the Stokes-Einstein equation gives the hydrodynamic radius R_H:

$$R_H = \frac{k_B T}{6\pi\eta D} \tag{S5}$$

With the Boltzmann constant k_B, absolute temperature T in K, and the dynamic viscosity of water η.

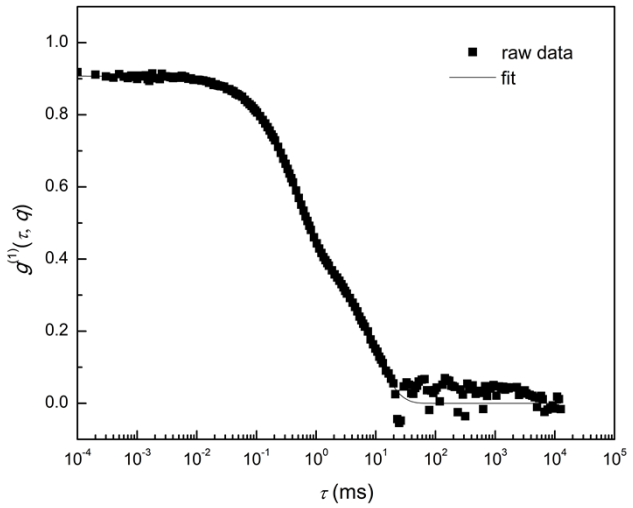


Figure S28: Auto correlation function of P(EG_{123}-*co*-$OlGE_7$) at a scattering angle of 30° plotted against τ.

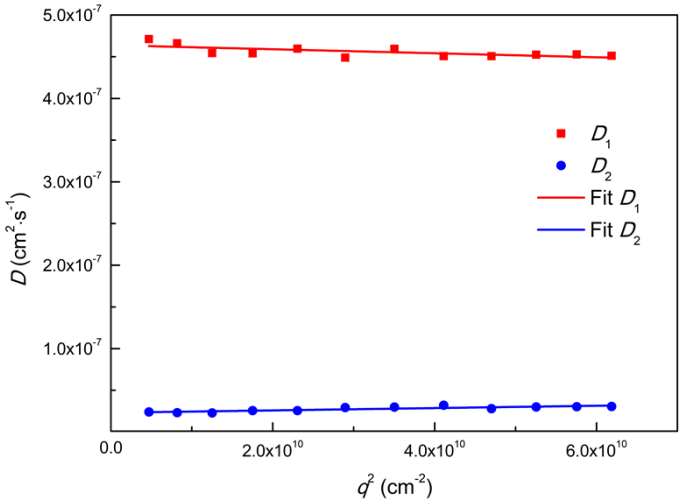


Figure S29: Diffusion coefficient plotted against the square of the scattering vector of the polymer P(EG_{123}-*co*-$OlGE_7$).

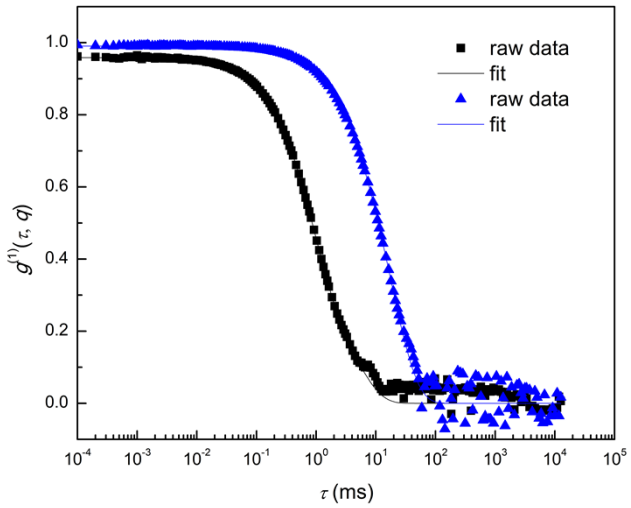


Figure S30: Auto correlation function of mPEG$_{45}$-*b*-POlGE$_{2.4}$ (black squares) and mPEG$_{45}$-*b*-POlGE$_{5.0}$ (blue triangles) at a scattering angle of 30° plotted against *τ*.

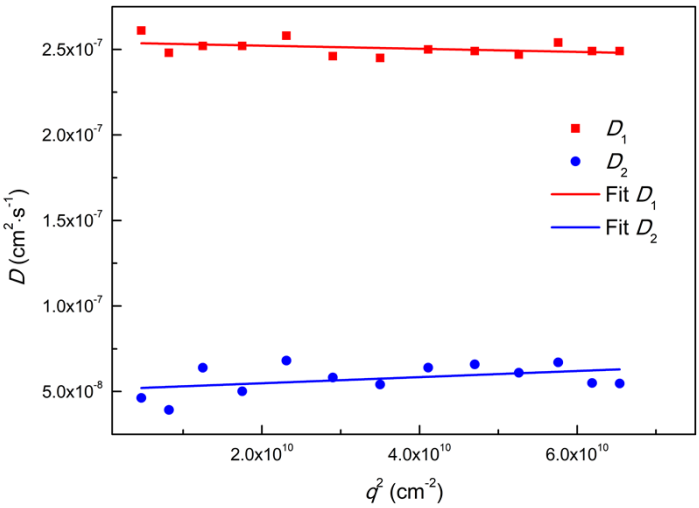


Figure S31: Diffusion coefficient plotted against the square of the scattering vector of the polymer mPEG$_{45}$-*b*-POlGE$_{2.4}$.

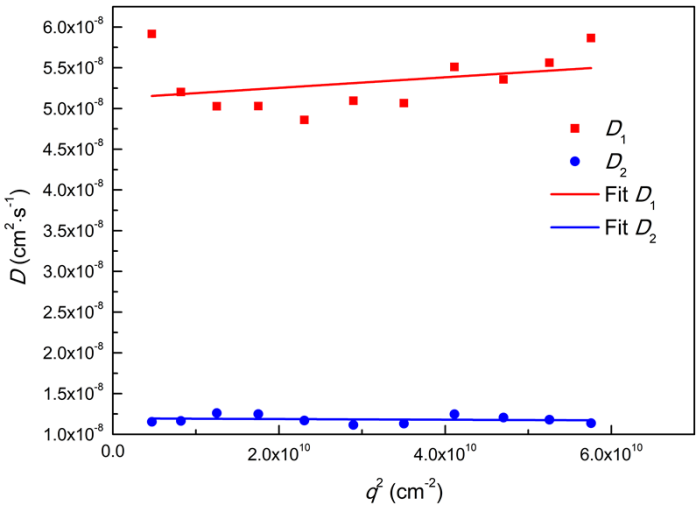


Figure S32: Diffusion coefficient plotted vs square of the scattering vector of the polymer mPEG$_{45}$-*b*-POlGE$_{5.0}$.

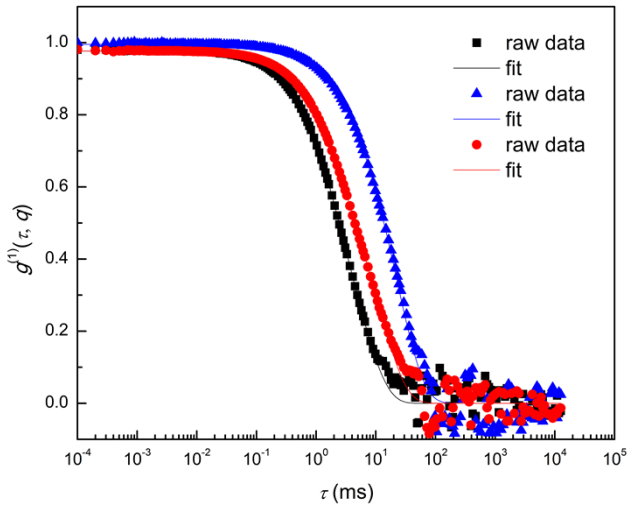


Figure S33: Auto correlation function of mPEG$_{114}$-*b*-POlGE$_{2.9}$ (black squares), mPEG$_{114}$-*b*-POlGE$_{5.8}$ (blue triangles) and mPEG$_{114}$-*b*-POlGE$_{7.3}$ (red circles) at a scattering angle of 30° plotted against *τ*.

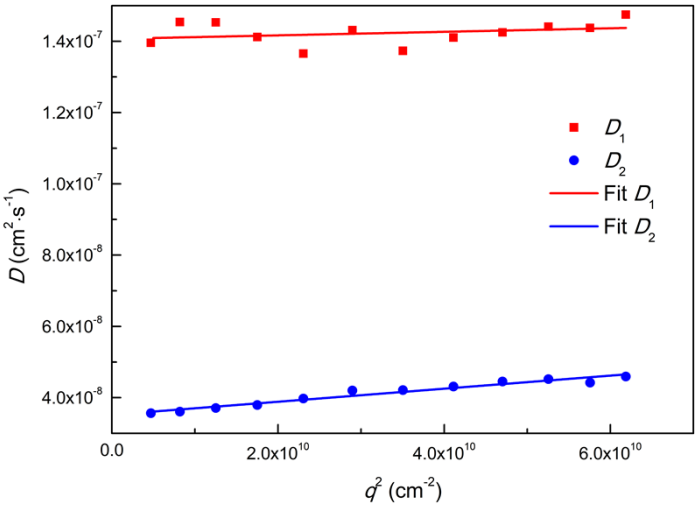


Figure S34: Diffusion coefficient plotted against the square of the scattering vector of the polymer mPEG$_{114}$-*b*-POlGE$_{2.9}$.

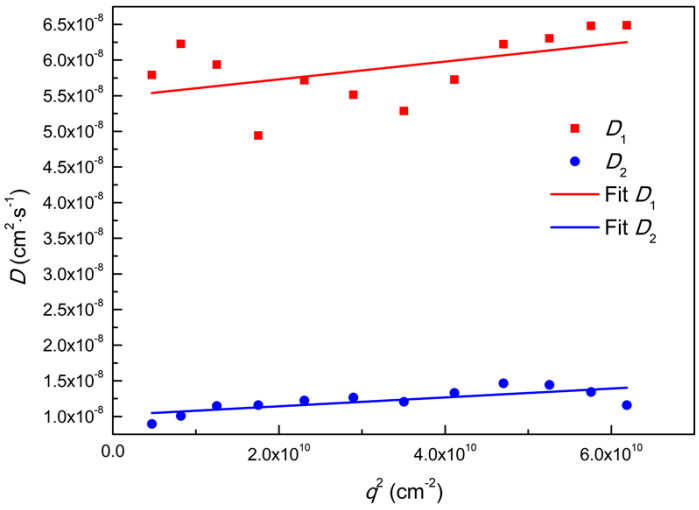


Figure S35: Diffusion coefficient plotted vs square of the scattering vector of the polymer mPEG$_{114}$-*b*-POlGE$_{5.8}$.

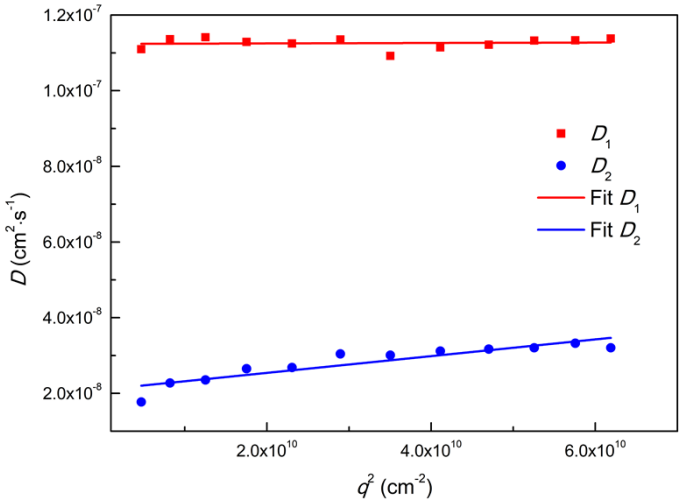


Figure S36: Diffusion coefficient plotted vs square of the scattering vector of the polymer mPEG$_{114}$-*b*-POlGE$_{7.3}$.

In Situ ^{1}H NMR Copolymerization Kinetics of OlGE and EO

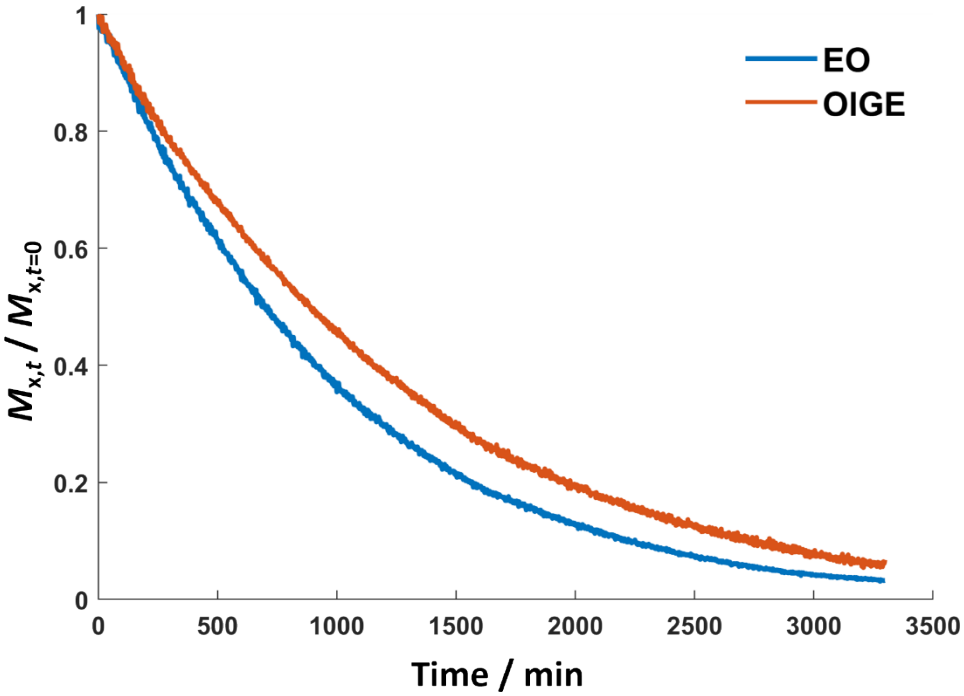


Figure S37: Time-conversion plot of the *in situ* ^{1}H NMR copolymerization kinetic study of EO with OlGE. (Solvent: DMSO-d_6/THF-d_8 1:5 (*V*/*V*), 40 °C.

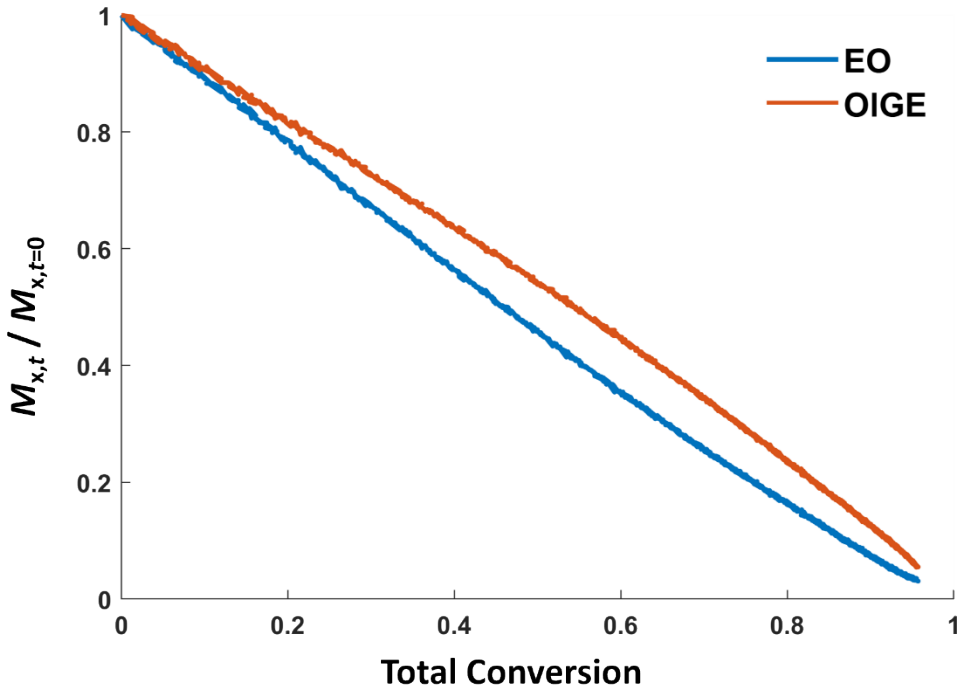


Figure S38: Individual versus total conversion of the *in situ* ^{1}H NMR copolymerization kinetic study of EO with OlGE. (Solvent: DMSO-d_6/THF-d_8 1:5 (*V*/*V*), 40 °C.

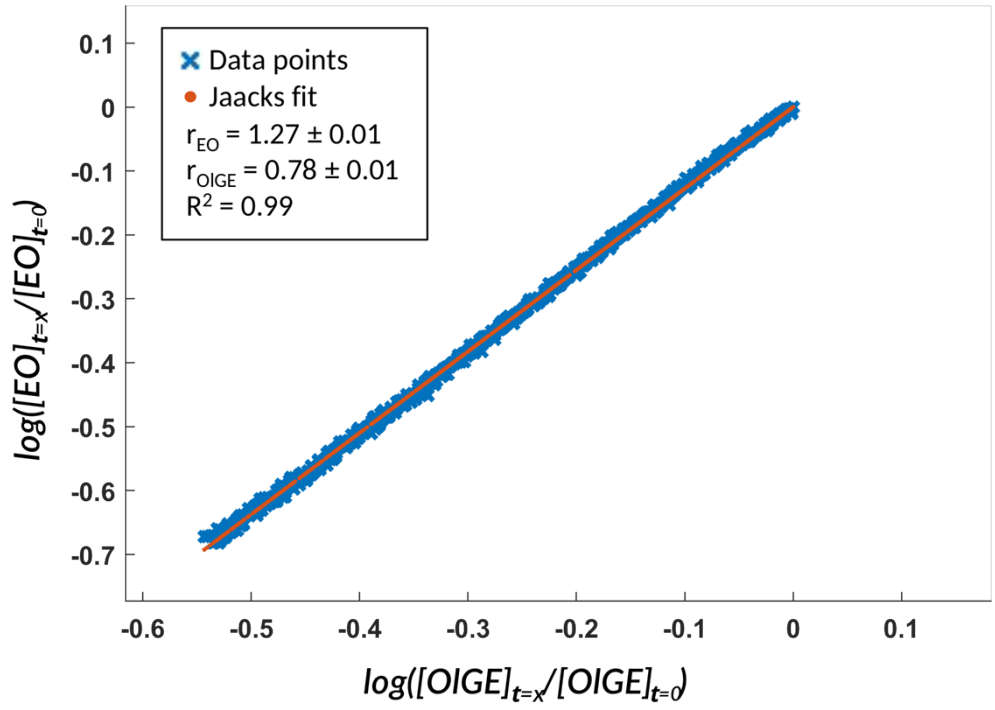


Figure S39: Jaacks fit of the *in situ* ^{1}H NMR copolymerization kinetics study of EO with OlGE. (Solvent: DMSO-d_6/THF-d_8 1:5 (*V*/*V*), 40 °C. Conversion threshold 75% to ensure significant signal to noise ratio of the epoxide functionalities.

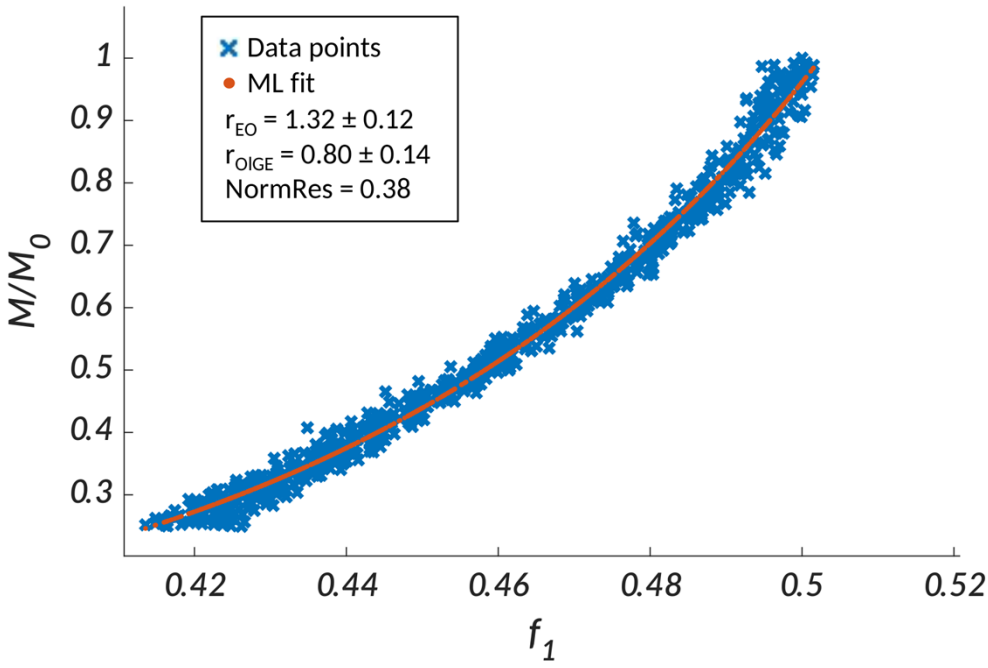


Figure S40: Meyer-Lowry fit of the *in situ* ^{1}H NMR copolymerization kinetic study of EO with OlGE. (Solvent: DMSO-d_6/THF-d_8 1:5 (*V*/*V*), 40 °C. Conversion threshold 75% to ensure significant signal to noise ratio of the epoxide functionalities.

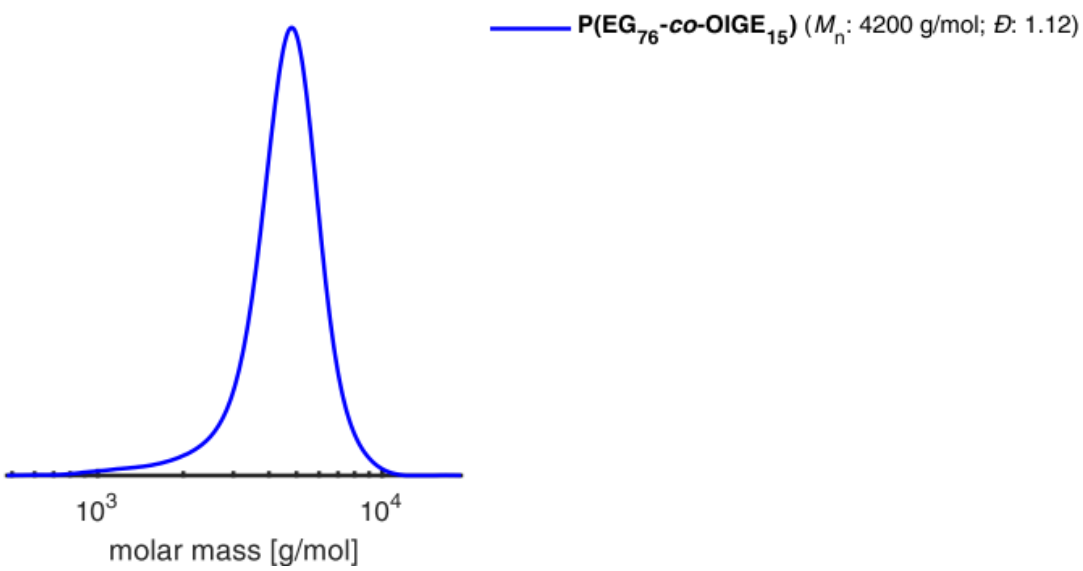


Figure S41: SEC trace of the P(EG_{76}-*co*-$OlGE_{15}$) copolymer formed in the *in situ* ^{1}H NMR kinetic study (RI detector, eluent: DMF, PEG calibration).

Post-polymerization Functionalization

Thiol-Ene Click

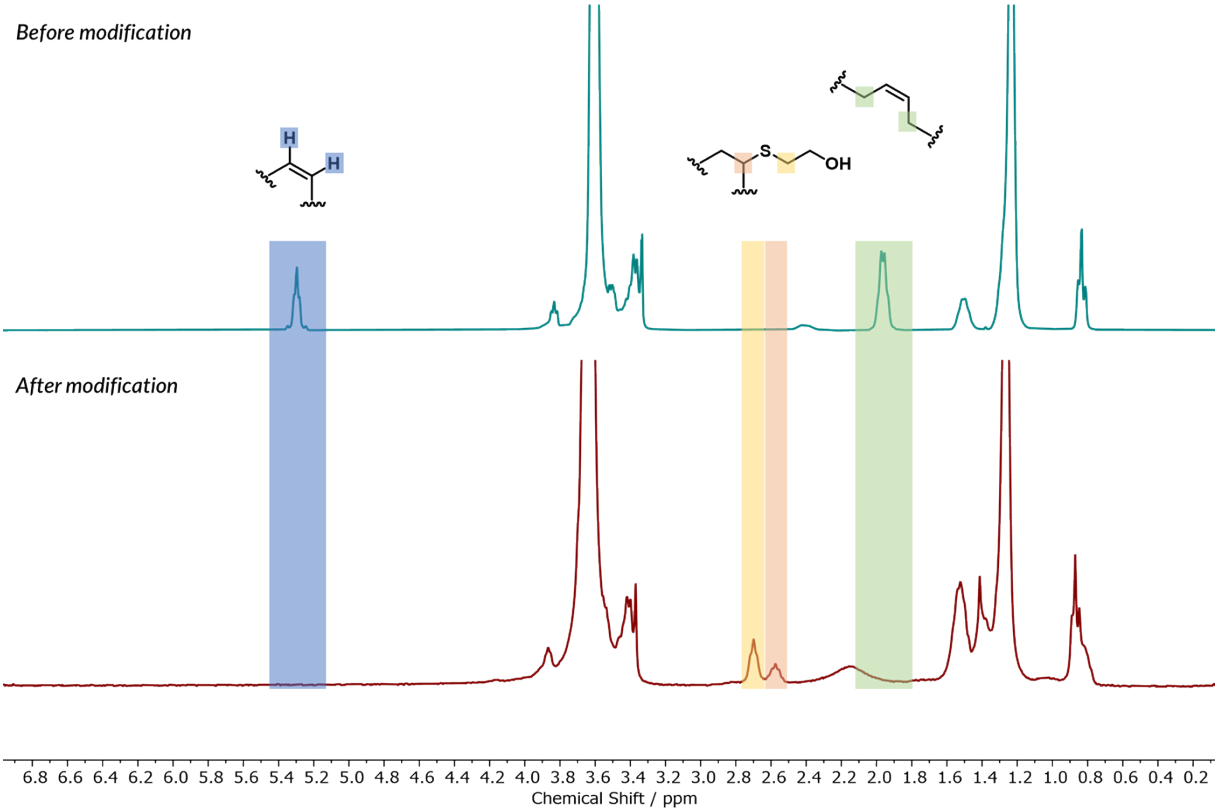


Figure S42: ^{1}H NMR spectrum of mPEG$_{114}$-*b*-POlGE$_{2.9}$ before/after modification via thiol-ene click (300 MHz, $CDCl_3$).

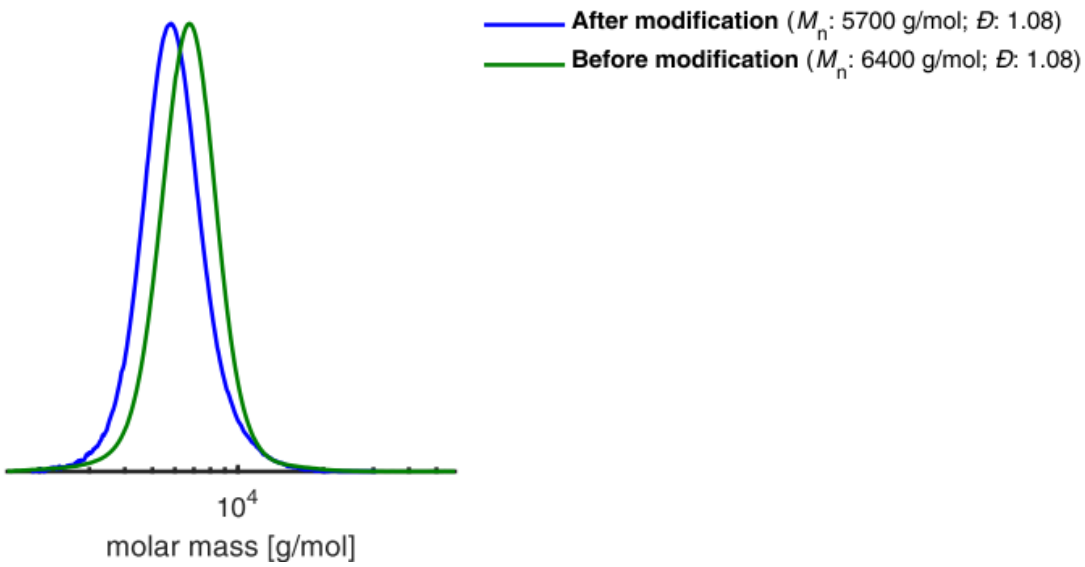


Figure S43: SEC traces of the polymer mPEG$_{114}$-*b*-POlGE$_{2.9}$ before (green) and after modification (blue) *via* thiol-ene click. Note that the apparent molecular weight decreases upon modification with thioglycol (eluent: THF, RI detector, PEG calibration).

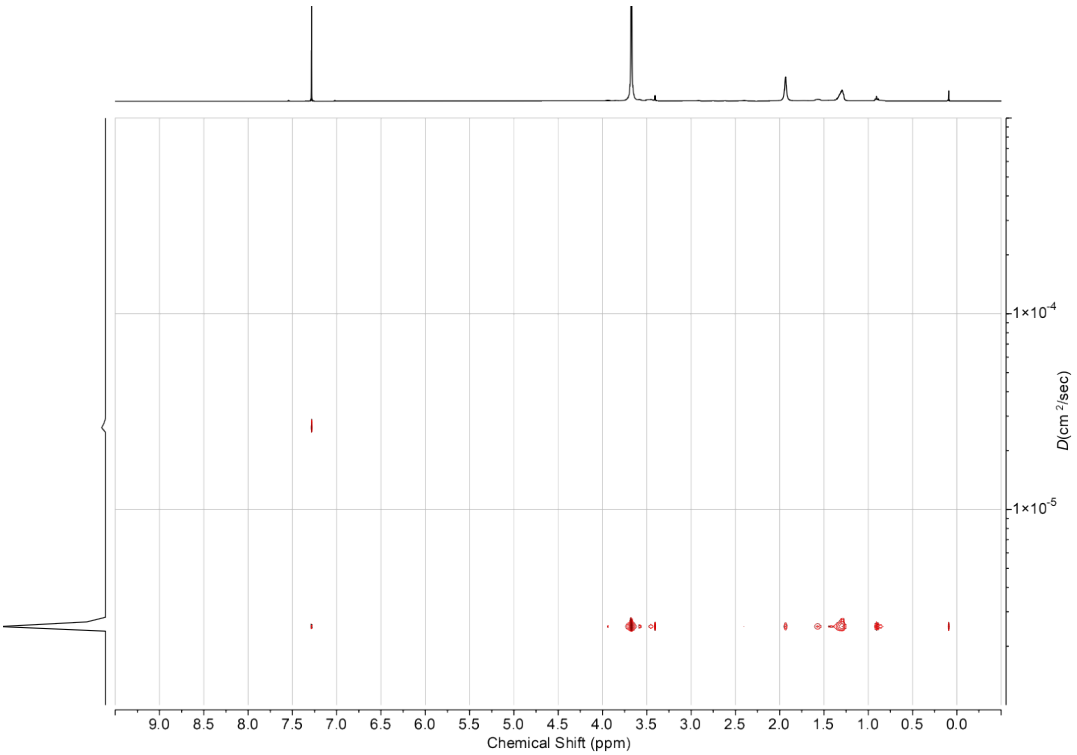


Figure S44: DOSY of modified mPEG$_{114}$-*b*-POlGE$_{2.9}$ with thioglycol (400 MHz, $CDCl_3$).

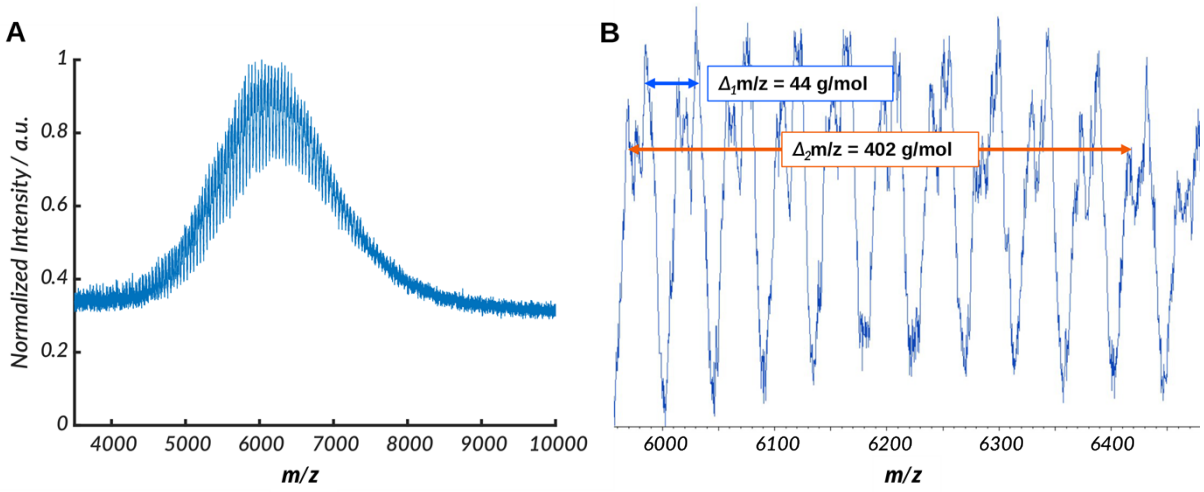


Figure S45: MALDI-ToF of $mPEG_{114}$-*b*-$POlGE_{2.9}$ functionalized with thioglycol (KTFA, linear mode, matrix: DCTB). Long arrow denotes the mass difference of the functionalized OlGE. Small arrow denotes the mass difference of the EO repeating unit. Note that the OlGE repeating unit (324 g/mol) was not found.

Hydrogenation via diimide from PADA

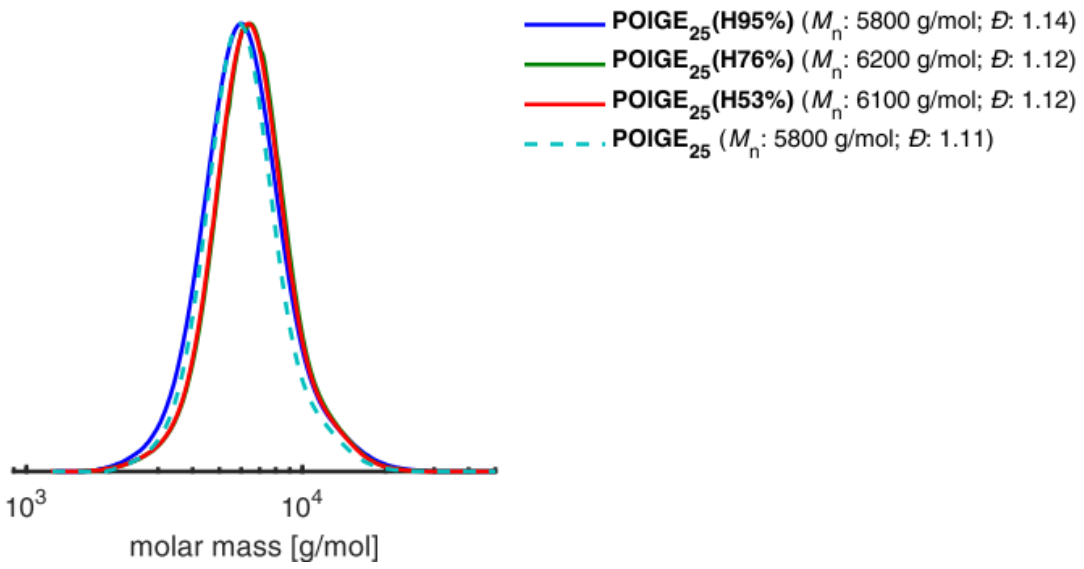


Figure S46: SEC trace of $POlGE_{25}$ and the respective hydrogenated Polymers (eluent: THF, RI detector, PEG calibration). The value of H denotes the degree of hydrogenation.

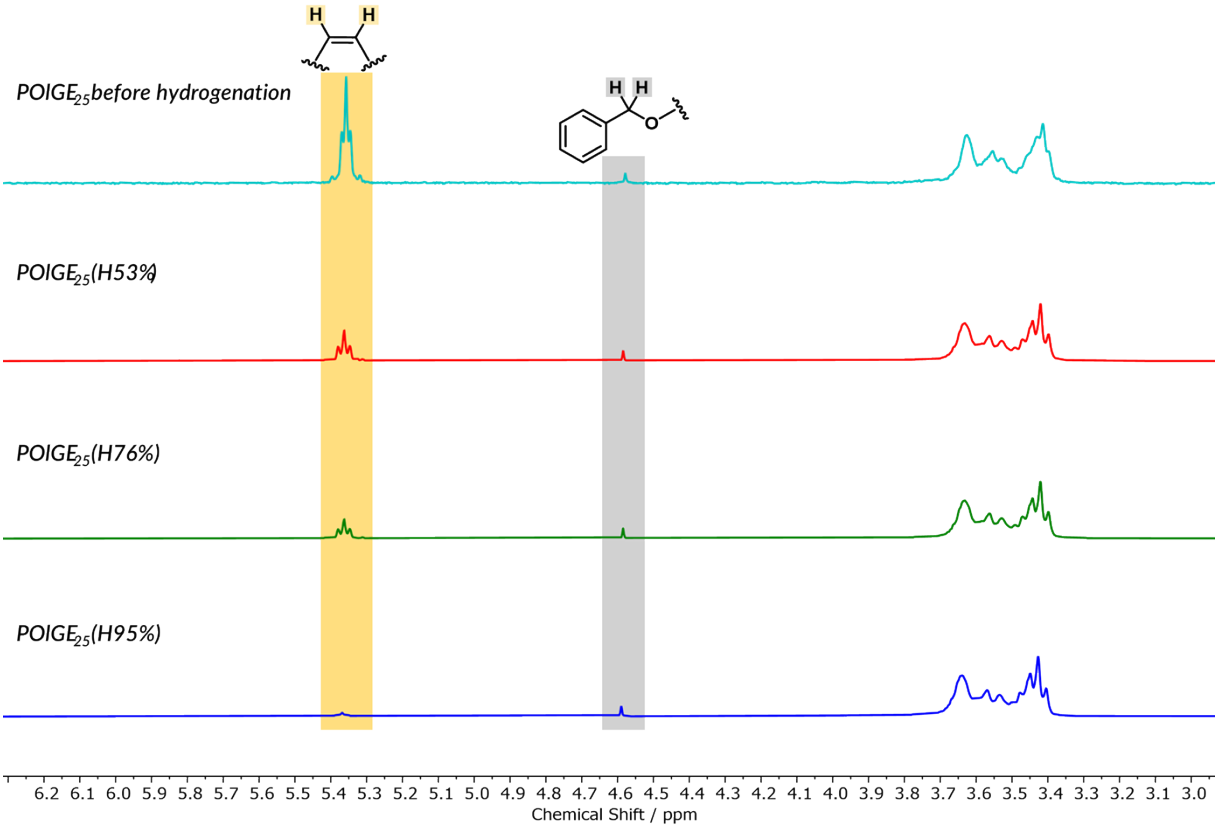


Figure S47: ^{1}H NMR spectra of POlGE$_{25}$ and the respective hydrogenated Polymers (400 MHz, $CDCl_3$). The value of H denotes the degree of hydrogenation.

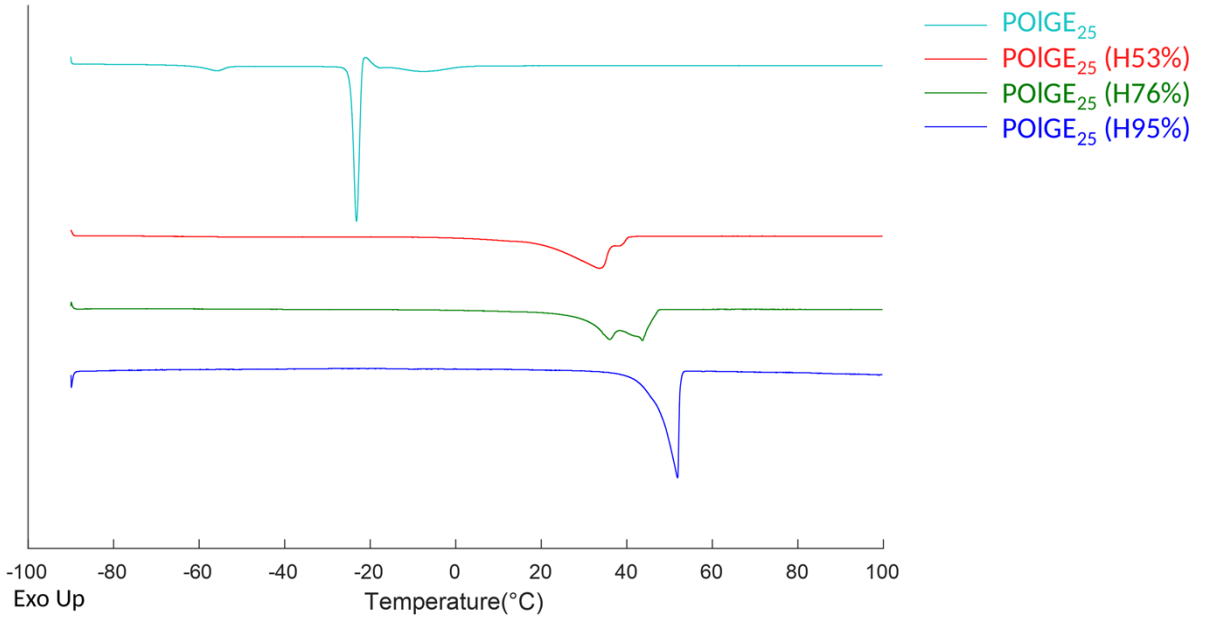


Figure S48: DSC thermograms of POlGE (partially) hydrogenated homopolymers and the respective precursor. Second heating curve, 1 K/min.

References

1 S. Schüttner, M. Krappel, M. Koziol, L. Marquart, I. Schneider, T. Sottmann and H. Frey, *Macromolecules*, 2023, **56**, 6928-6940.

2 H. G. O. Becker, *Organikum. Organisch-chemisches Grundpraktikum*, Wiley-VCH, Weinheim, 21st edn., 2001.

3 G. Mouzin, H. Cousse, J.-P. Rieu and A. Duflos, *Synthesis*, 1983, **1983**, 117–119.

4 J. Herzberger, D. Leibig, J. C. Liermann and H. Frey, *ACS Macro Lett.*, 2016, **5**, 1206–1211.

5 M. Steube, T. Johann, M. Plank, S. Tjaberings, A. H. Gröschel, M. Gallei, H. Frey and A. H. E. Müller, *Macromolecules*, 2019, **52**, 9299–9310.

6 J. T. Groves and K. W. Ma, *J. Am. Chem. Soc.*, 1977, **99**, 4076–4082.

7 J. W. Hamersma and E. I. Snyder, *J. Org. Chem.*, 1965, **30**, 3985–3988.

8 S. Schüttner, G. M. Linden, E. C. Hoffmann, P. Holzmüller and H. Frey, *Polym. Chem.*, 2025, 374–385.