Supporting Information

Polymerization of Long Chain Alkyl Glycidyl Ethers: A Platform for Micellar Gels with Tailor-Made Melting Points

*Patrick Verkoyen[1], Tobias Johann[1,2], Jan Blankenburg[1,3], Christian Czysch[1], Holger Frey[*1]*

[1]Institute of Organic Chemistry, Johannes Gutenberg-University Mainz, Duesbergweg 10-14, D-55128 Mainz, Germany

[2]Max Planck Graduate Center, Forum Universitatis 2, D-55122 Mainz, Germany

[3]Graduate School Materials Science in Mainz, Staudinger Weg 9, D-55128 Mainz, Germany

Figure S1. Image of the custom-made press with PEEK and Teflon inlays (left) for polymer processing to hydrogel samples.

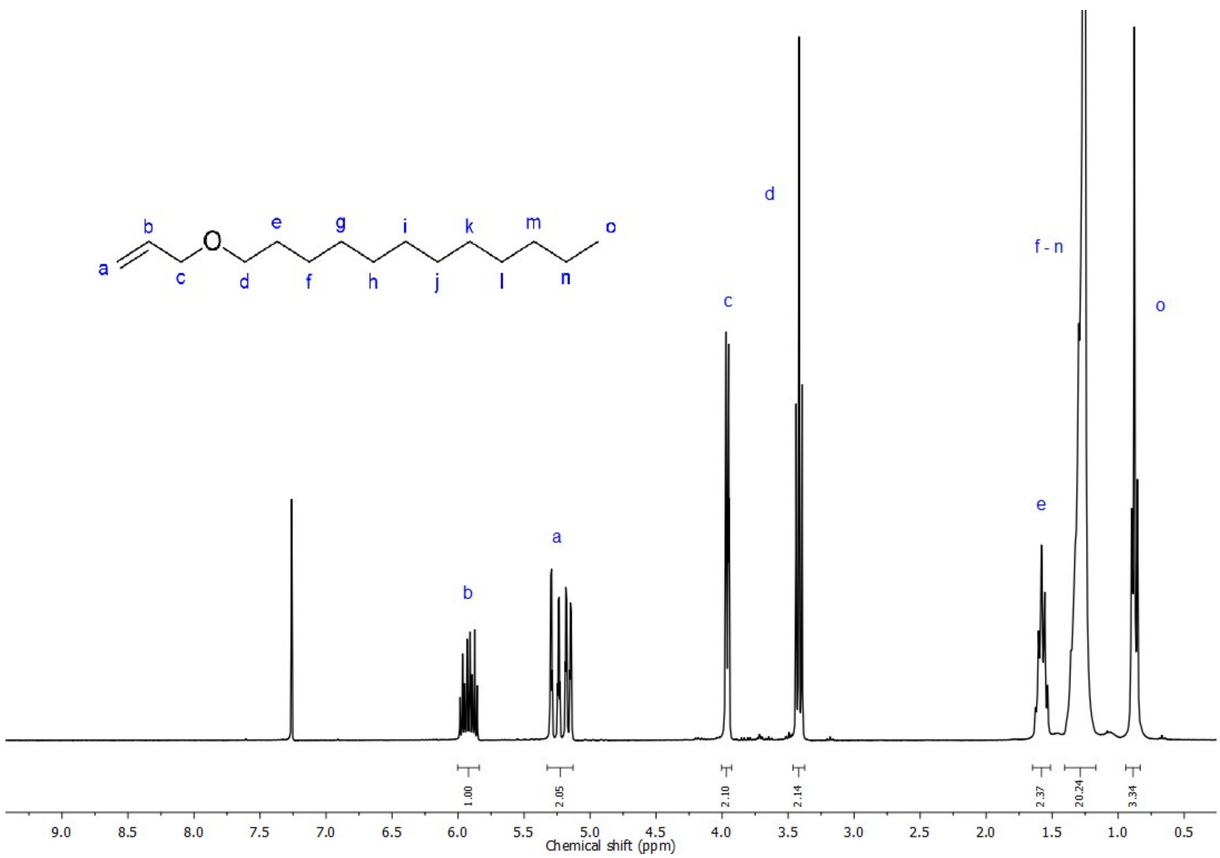

Figure S2. ^{1}H NMR spectrum (300 MHz, chloroform-d) of dodecyl allyl ether.

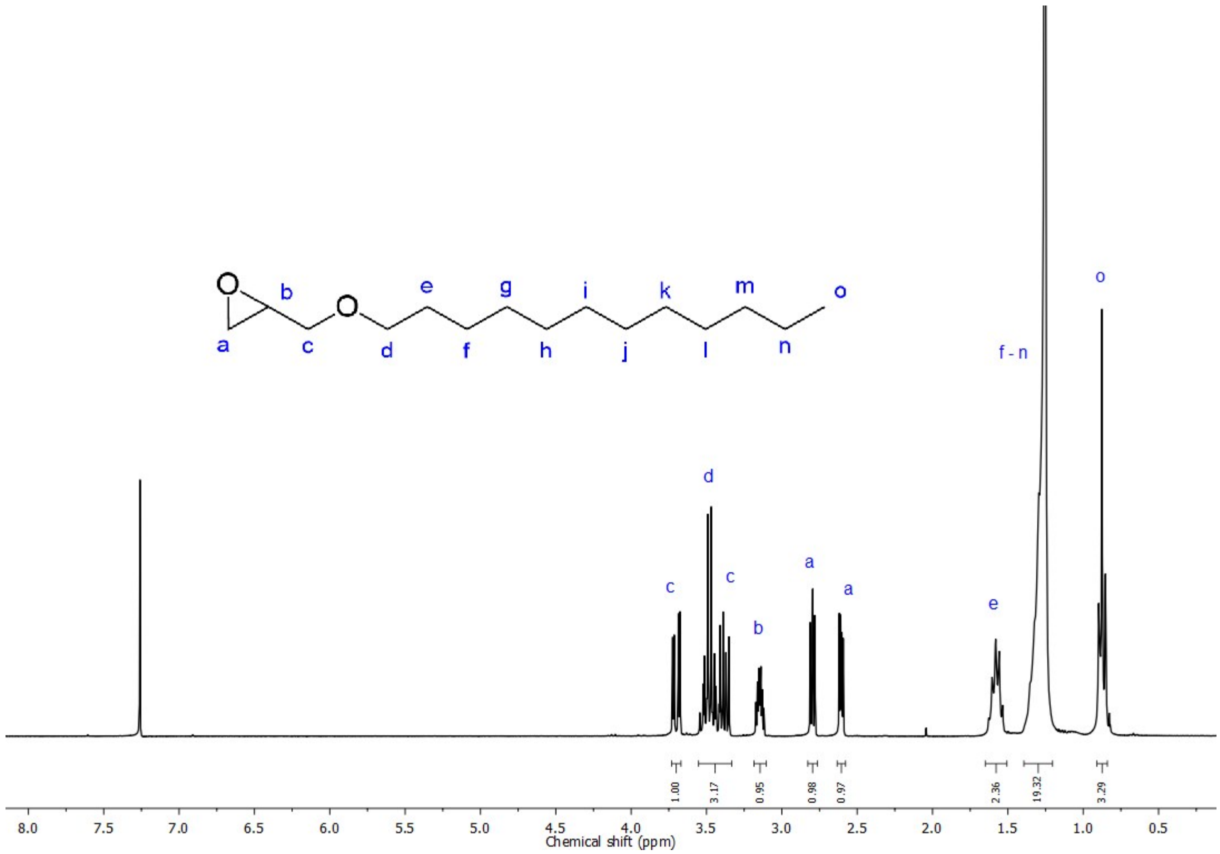

Figure S3. ^{1}H NMR spectrum (300 MHz, chloroform-d) of dodecyl glycidyl ether.

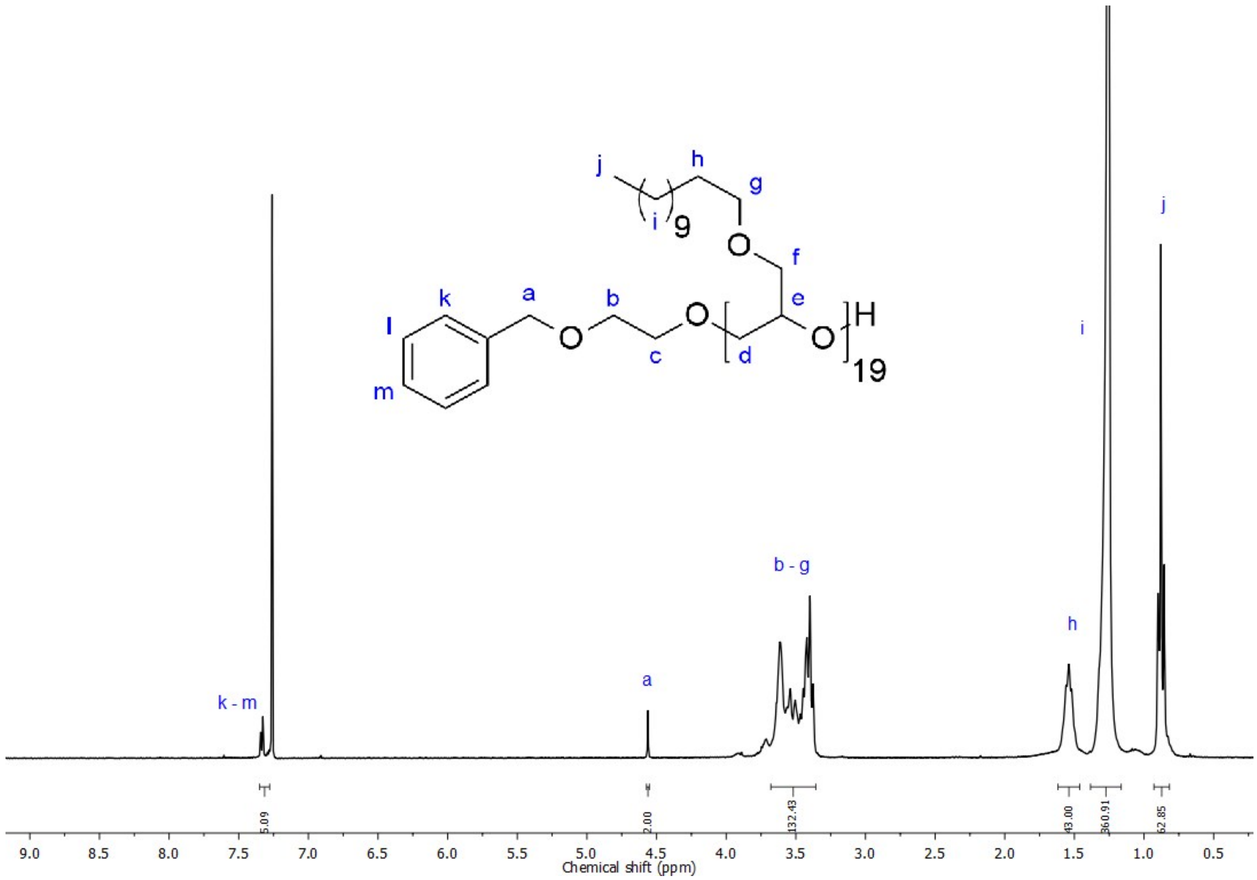

Figure S4. ^{1}H NMR spectrum (300 MHz, chloroform-d) of BnO-PC12-AlkGE$_{19}$.

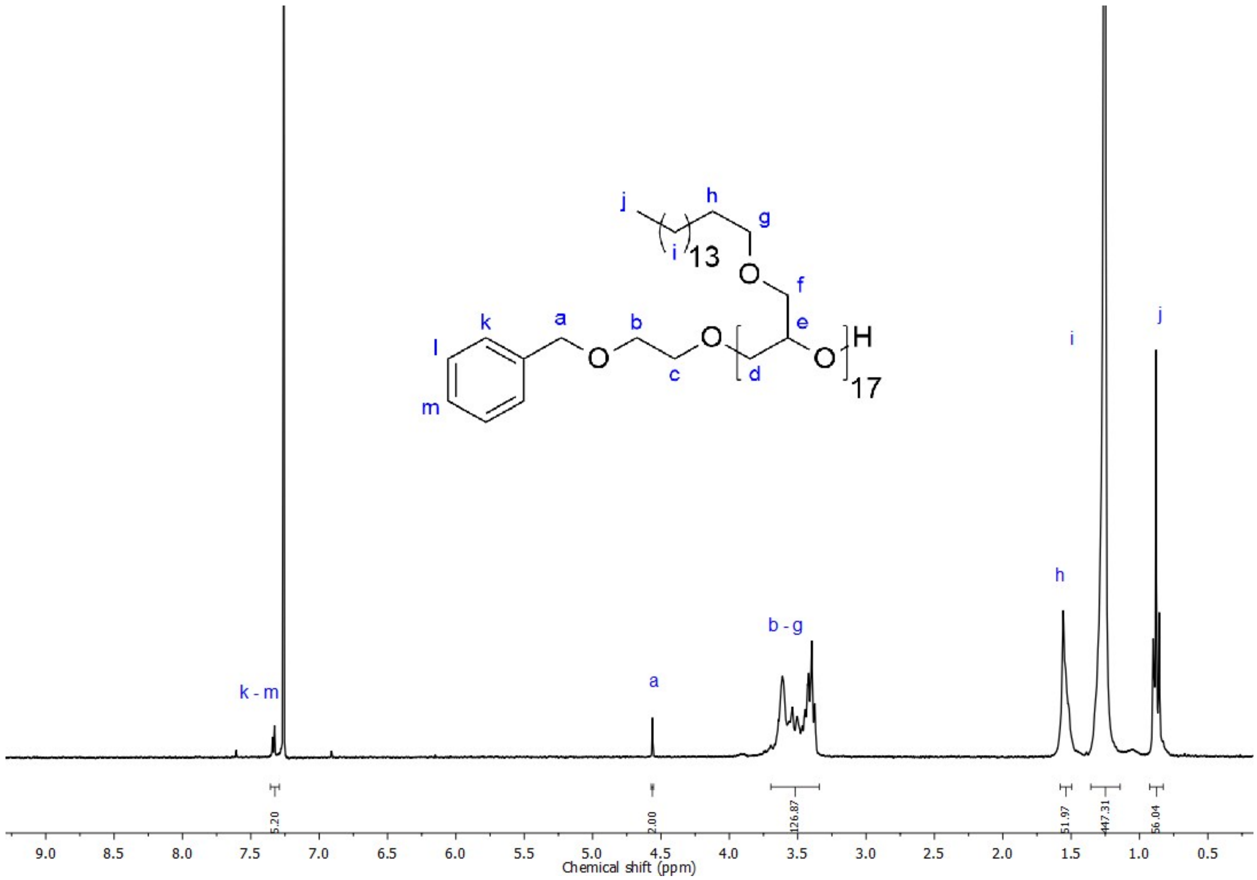

Figure S5. ^{1}H NMR spectrum (300 MHz, chloroform-d) of BnO-PC16-AlkGE$_{17}$.

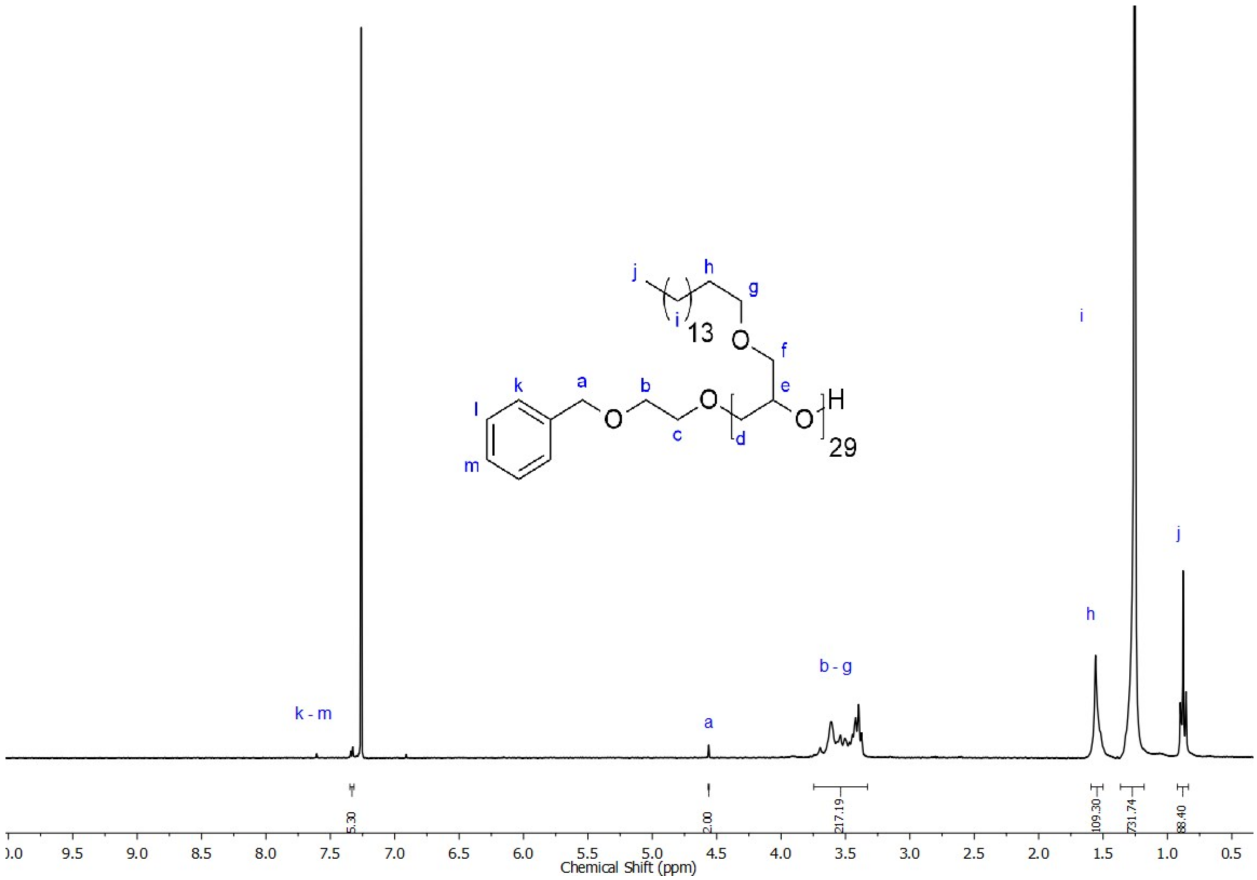

Figure S6. ^{1}H NMR spectrum (300 MHz, chloroform-d) of BnO-PC16-AlkGE$_{29}$.

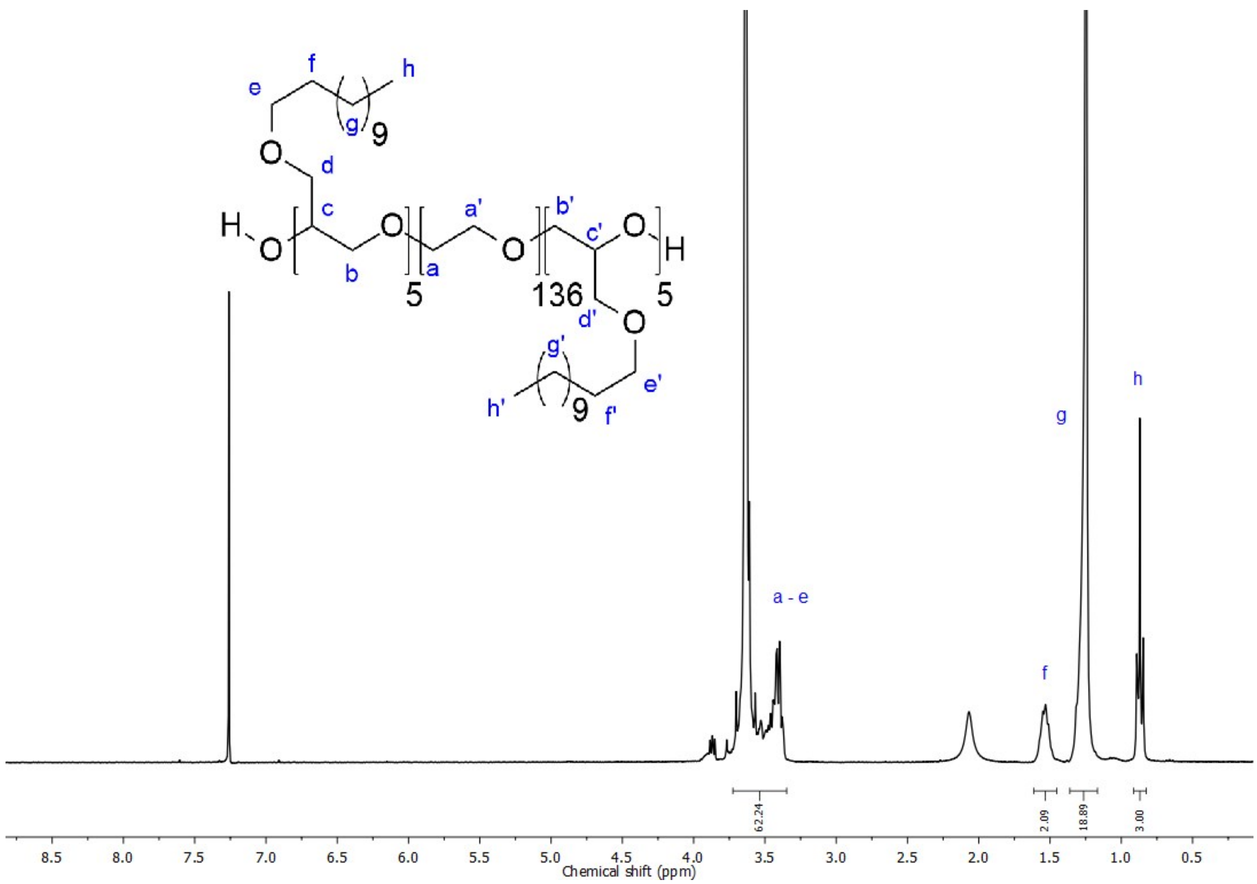

Figure S7. [1]H NMR spectrum (300 MHz, chloroform-d) of PC12$_5$-*b*-PEG$_{136}$-*b*-PC12$_5$.

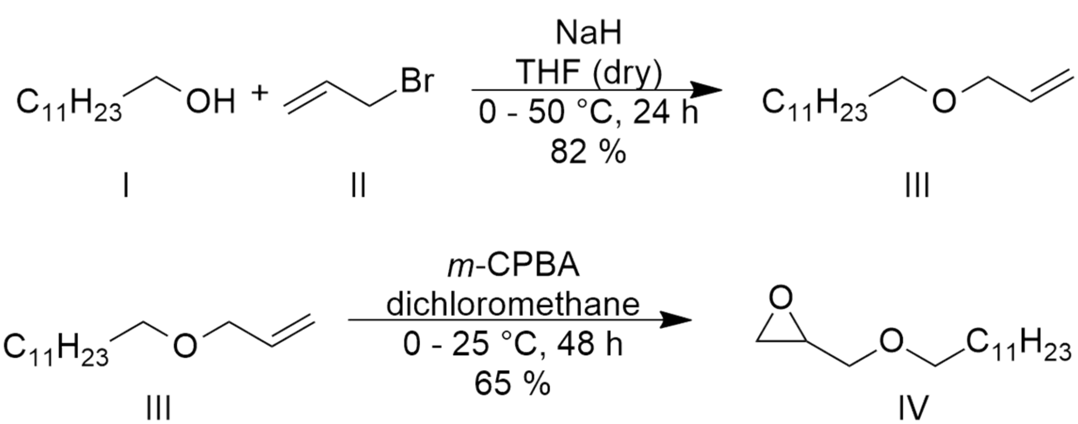

Figure S8. Synthetic procedure for the preparation of long-chain alkyl glycidyl ethers.

The synthetic sequence shown in **Figure S8** is a modified literature procedure.[1]

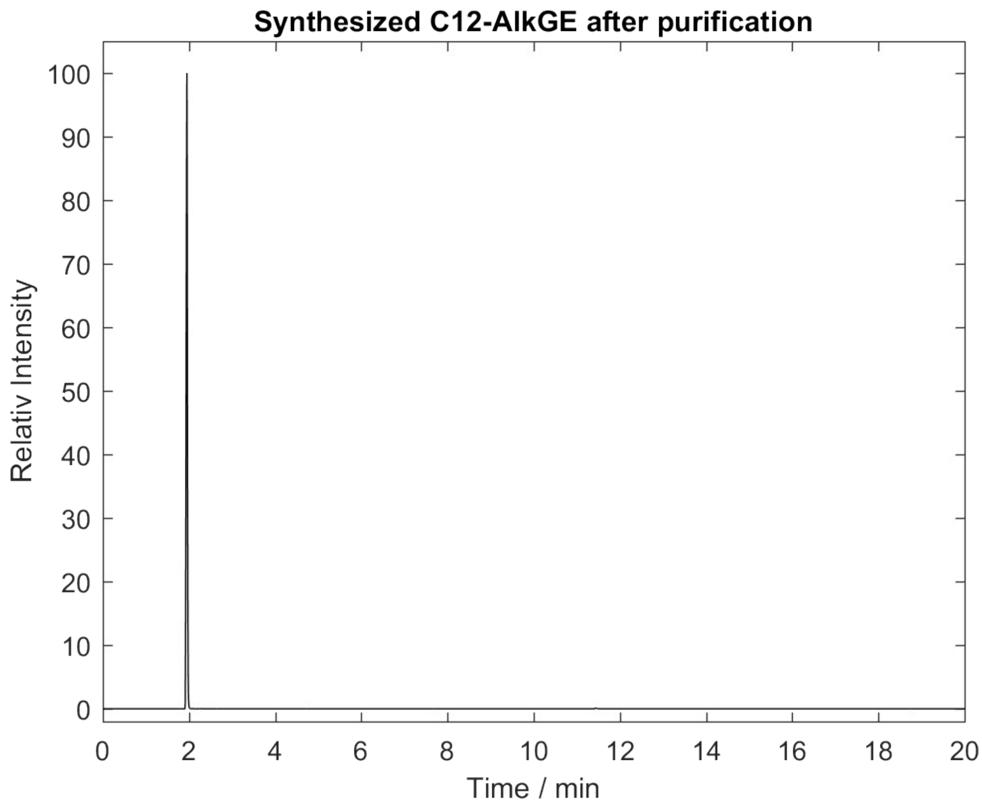

Figure S9. GC-measurement of the synthesized dodecyl glycidyl ether.

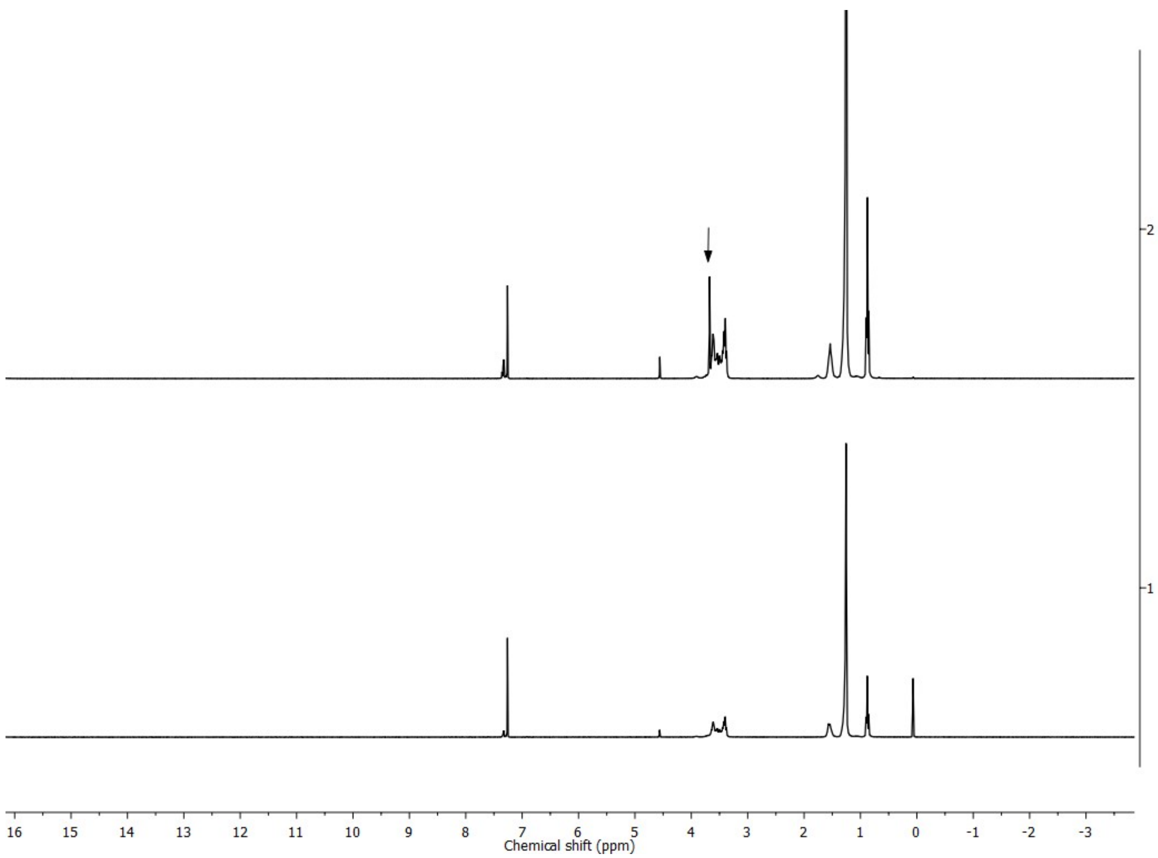

Figure S10. ^{1}H NMR spectrum (300 MHz, chloroform-d) of BnO-PC12-AlkGE$_{17}$ before (2) and after (1) removal of crown ether (indicated by arrow) via work-up procedure.

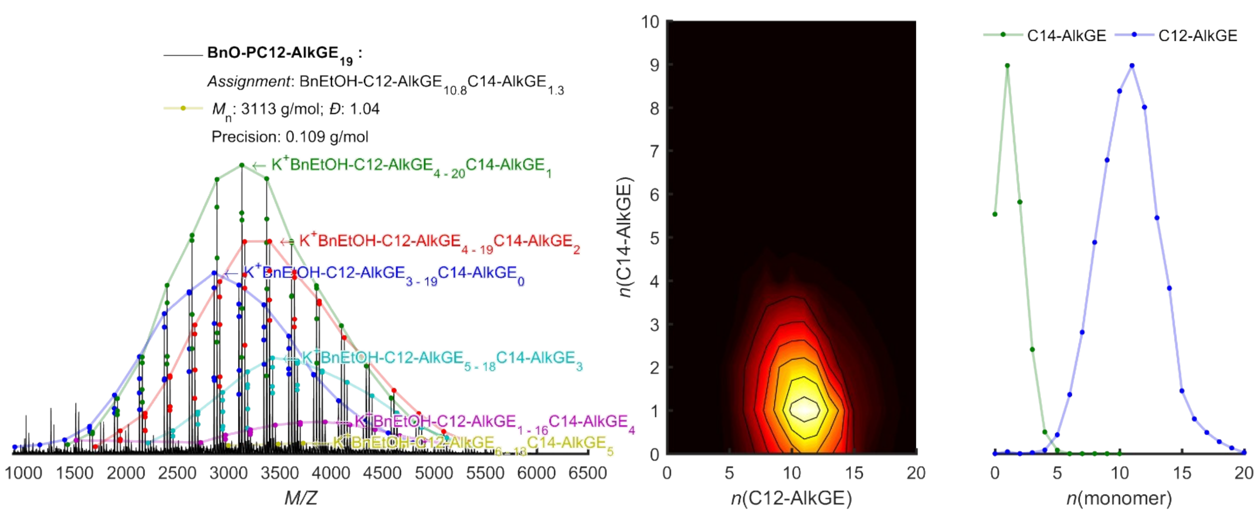

Figure S11. MALDI-ToF measurement of BnO-PC12-AlkGE, using the purchased C$_{12}$-AlkGE. Impurities of C$_{14}$-AlkGE are indicated (left), and all peaks can be assigned (right).

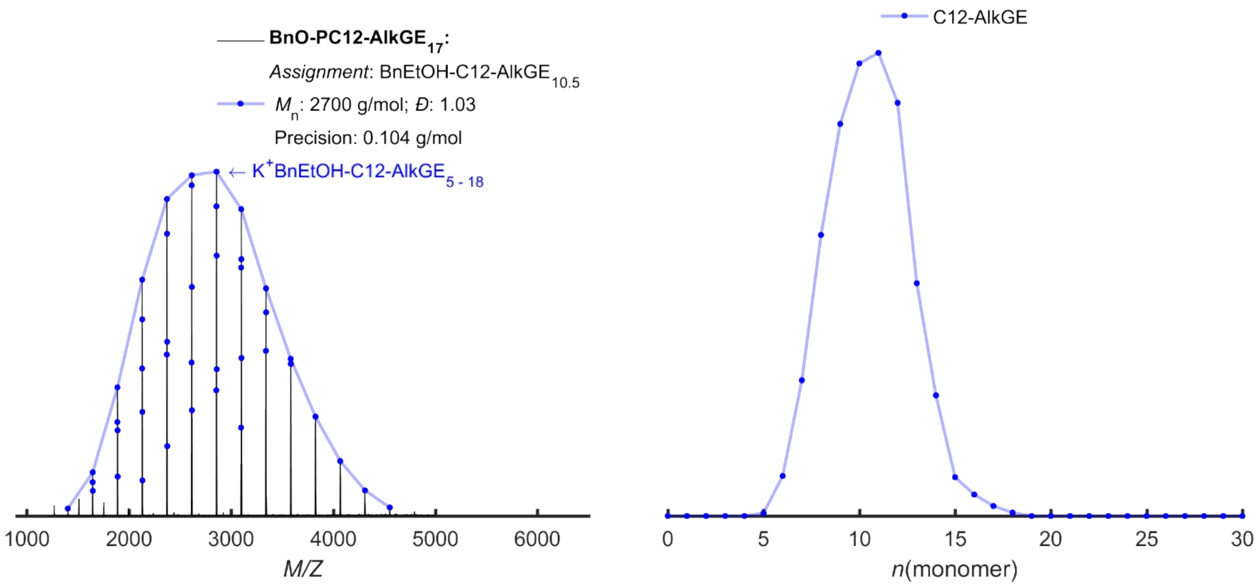

Figure S12. MALDI-ToF measurement of BnO-PC12-AlkGE$_{17}$, using the synthesized C$_{12}$-AlkGE.

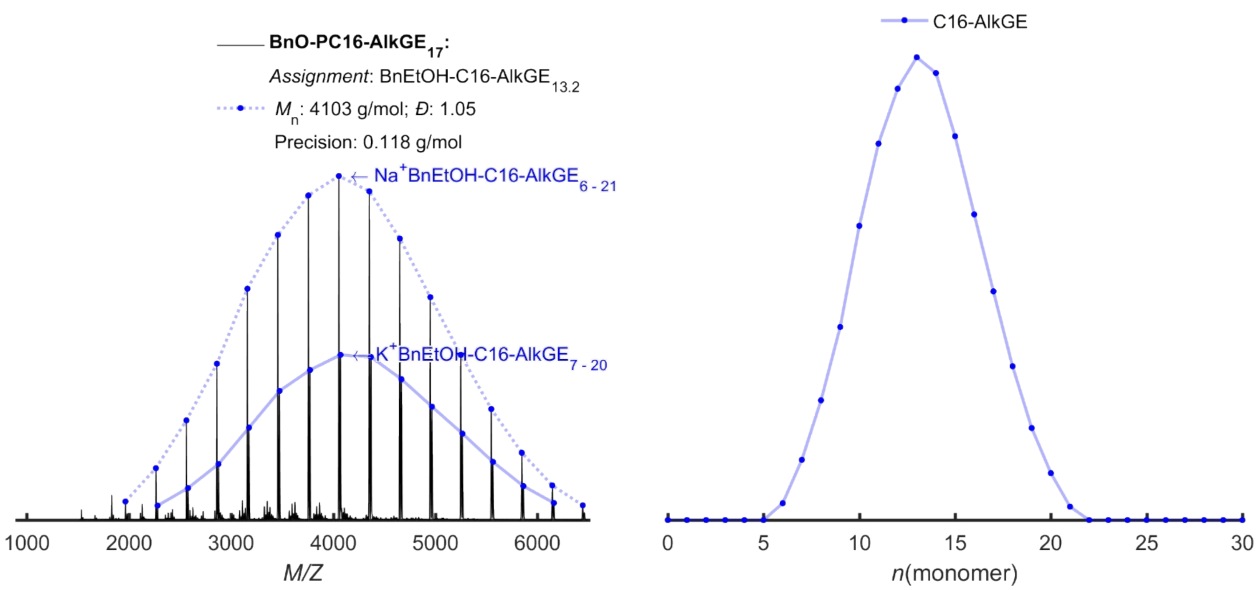

Figure S13. MALDI-ToF measurement of BnO-PC16-AlkGE$_{17}$, using the purified C$_{16}$-AlkGE.

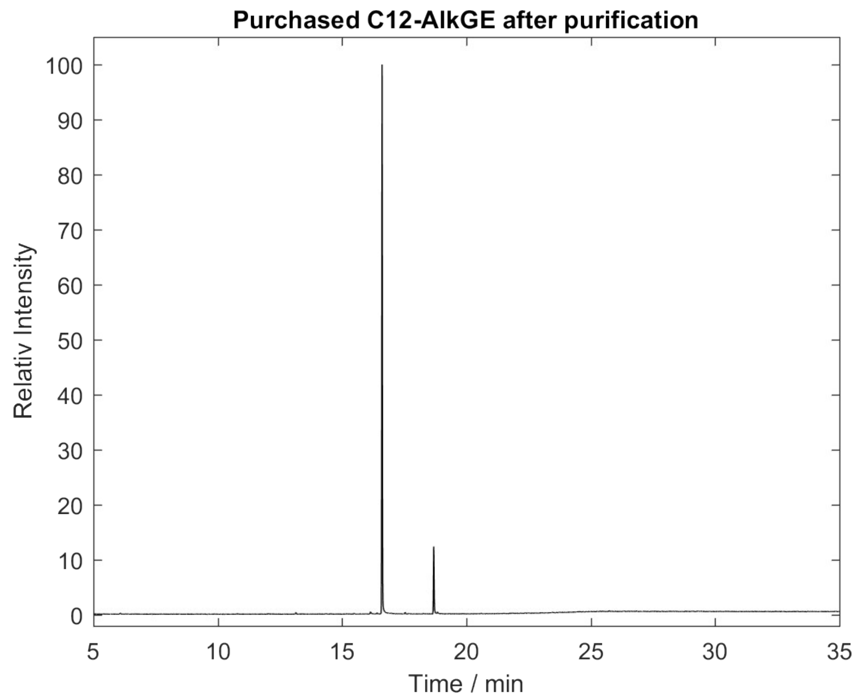

Figure S14. GC-measurement of commercial C_{12}-AlkGE after purification (retention time: 16.6 min), showing C_{14}-AlkGE impurity (retention time: 18.7 min).

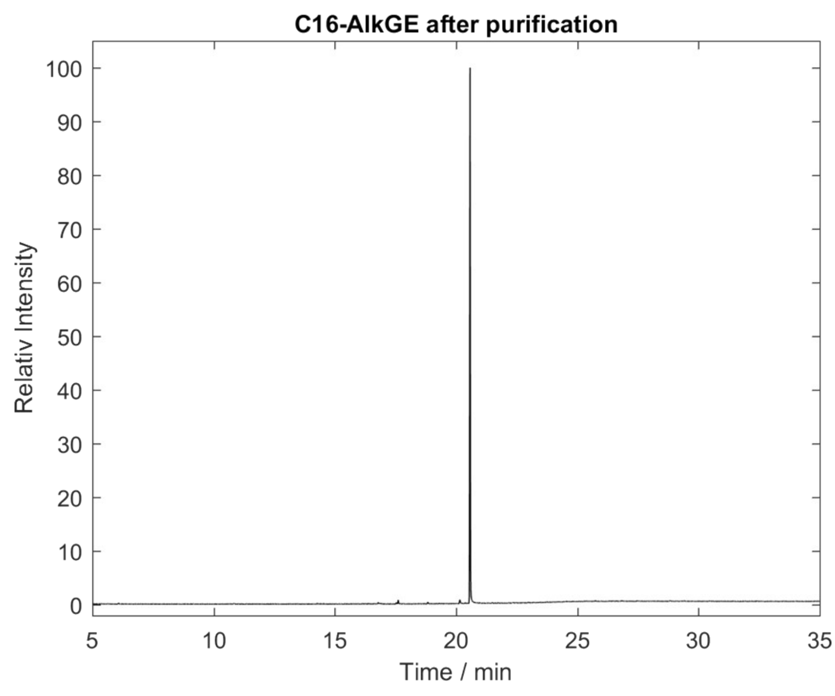

Figure S15. GC-measurement of purchased C_{16}-AlkGE after purification.

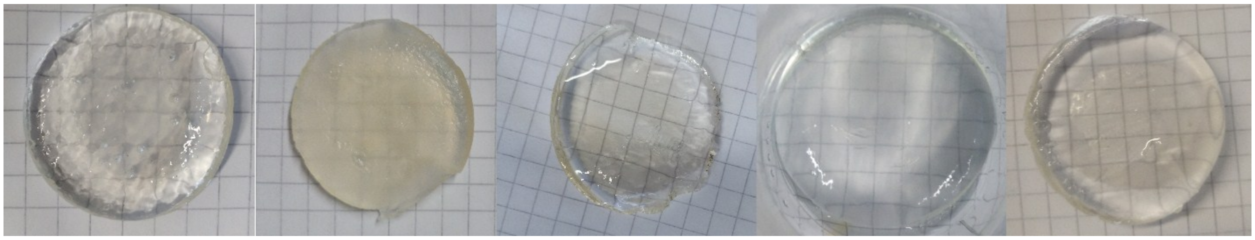

Figure S16. Images of hydrogel samples after swelling in water/ethanol mixture (50/50 wt%). From left: $PC16_5$-*b*-PEG_{136}-*b*-$PC16_5$, $PC16_6$-*b*-PEG_{227}-*b*-$PC16_6$, $PC12_5$-*b*-PEG_{227}-*b*-$PC12_5$, $PC16_5$-*b*-PEG_{454}-*b*-$PC16_5$, $PC12_6$-*b*-PEG_{454}-*b*-$PC12_6$.

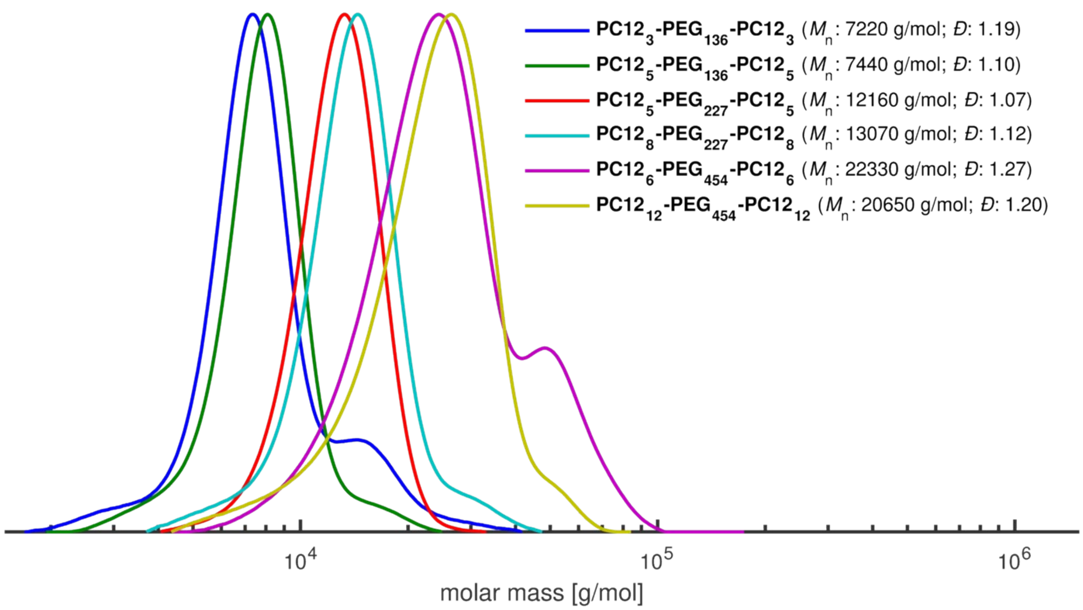

Figure S17. SEC traces of the prepared triblock copolymers using C_{12}-AlkGE. (eluent: DMF, calibration: PEG standards)

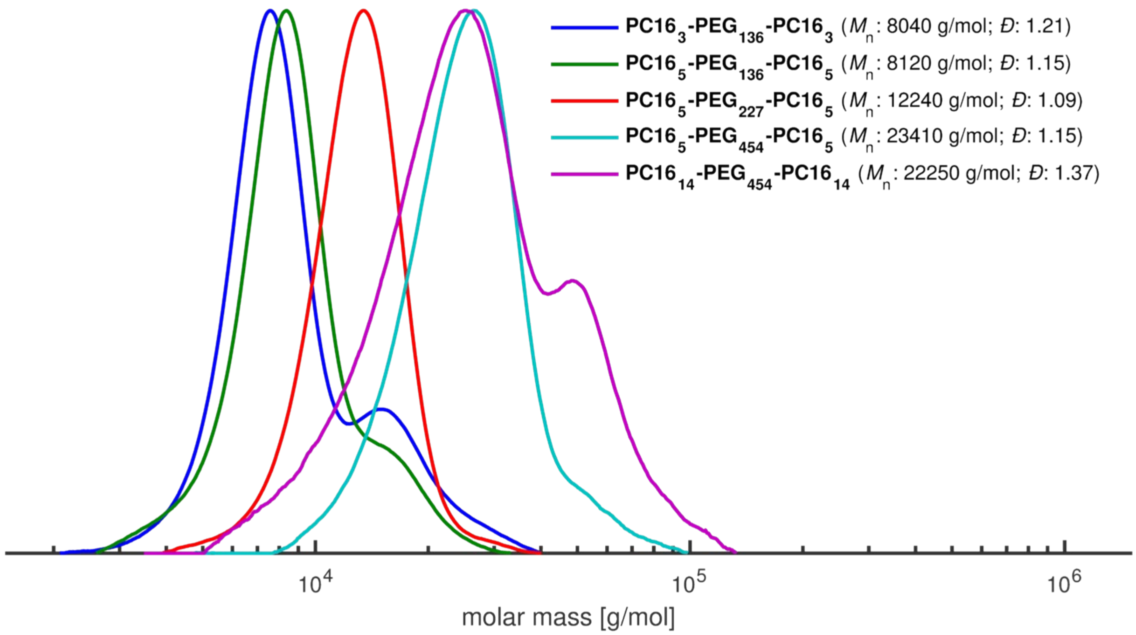

Figure S18. SEC traces of the prepared triblock copolymers using C_{16}-AlkGE. (eluent: DMF, calibration: PEG standards).

Figures S17 and S18 show the SEC traces of the prepared ABA triblock copolymers. Some of the traces show a second mode in the range of the exact double molecular weight. Additionally, not all samples synthesized could be measured using DMF as an eluent, as it is detailed in the manuscript text. The appearance of additional signals in the range of the twofold molecular weight suggests an aggregation during the elution procedure. This can be explained by the low solubility of the samples in DMF. The measured molecular weights show good agreement with the targeted molecular weights when determined by ^1H NMR.

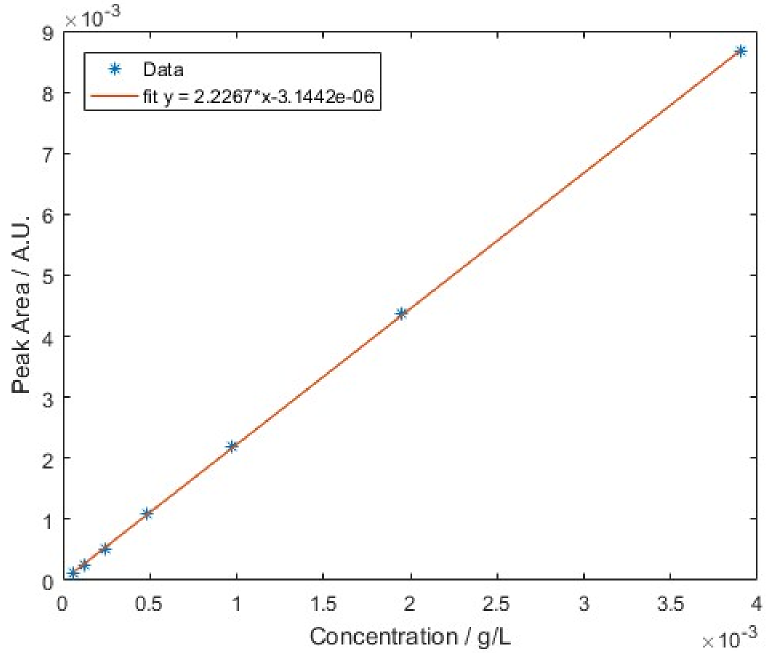

Figure S19. Linear fit of peak area of different Nile Red concentrations for calibration. (injection volume: 20 μL, eluent: hexane/chloroform, 20/80)

Using the respective fit equation, calculation of the Nile Red concentrations and amount of Nile Red incorporated in the entire gels is possible. Subsequently, the loading efficiencies can be calculated.

Table S1. Concentration values of Nile Red in the prepared hydrogels calculated by linear regression using 0.5 mL of a THF/Nile Red solution (concentration = 0.1 g/L) as initial solvent.

Polymer sample	Concentration in sample (20 μL injection) / g/L Peak area	Weight of the measured sample (mg)	Total weight of the gel (mg)
PEG_{227}	0.0000081	400	-
$PC12_3$-*b*-PEG_{136}-*b*-$PC12_3$	0.000035542	48	466
$PC12_5$-*b*-PEG_{136}-*b*-$PC12_5$	0.000068988	54	303
$PC12_5$-*b*-PEG_{227}-*b*-$PC12_5$	0.00019961	33	512
$PC12_8$-*b*-PEG_{227}-*b*-$PC12_8$	0.0011	38	370
$PC12_6$-*b*-PEG_{454}-*b*-$PC12_6$	0.00040532	58	560
$PC12_{12}$-*b*-PEG_{454}-*b*-$PC12_{12}$	0.00067191	53	471
$PC16_3$-*b*-PEG_{136}-*b*-$PC16_3$	0.000097287	65	531
$PC16_5$-*b*-PEG_{136}-*b*-$PC16_5$	0.00032	64	224
$PC16_6$-*b*-PEG_{227}-*b*-$PC16_6$	0.000069695	48	335
$PC16_9$-*b*-PEG_{227}-*b*-$PC16_9$	0.000062748	39	280
$PC16_5$-*b*-PEG_{454}-*b*-$PC16_5$	0.00089667	48	580
$PC16_{14}$-*b*-PEG_{454}-*b*-$PC16_{14}$	0.00067191	42	340

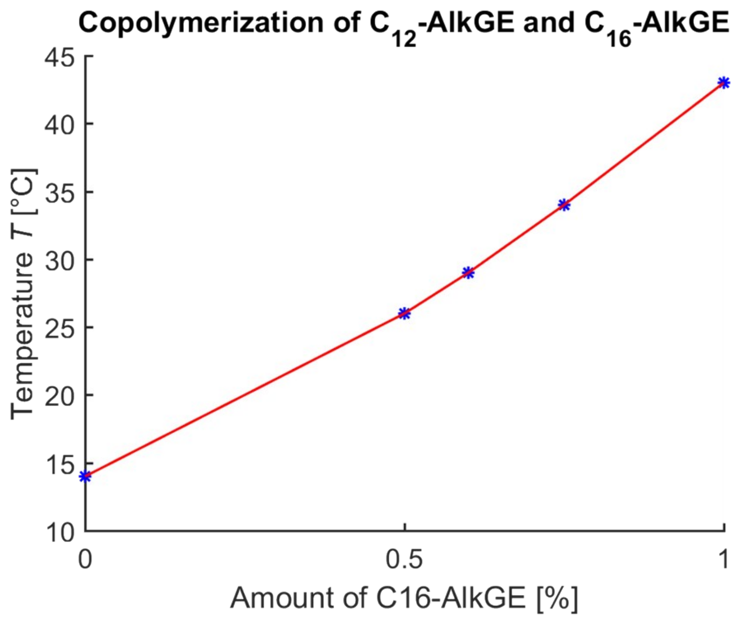

Figure S20. Trend of the copolymer melting temperatures when copolymerizing different monomer ratios of C_{12}-AlkGE and C_{16}-AlkGE. Blue dots represent measured melting points, the red line is extrapolated.

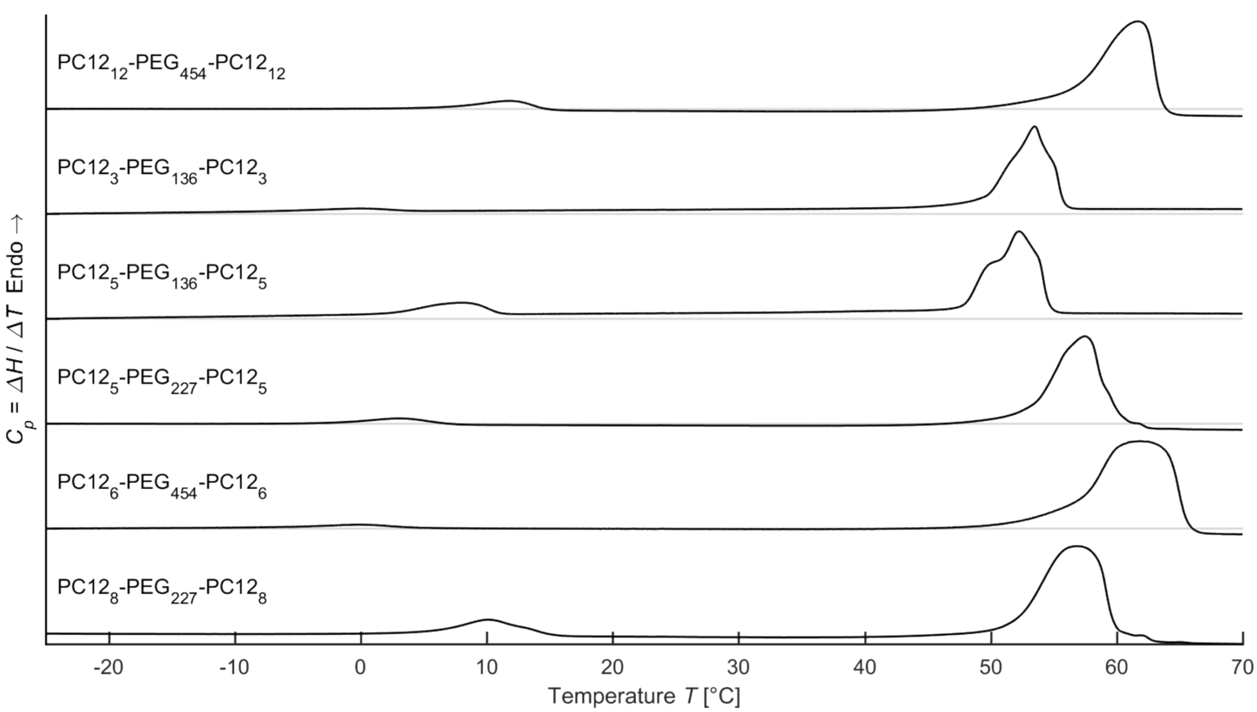

Figure S21. DSC-measurements of triblock copolymers containing PC12-AlkGE-blocks (in bulk).

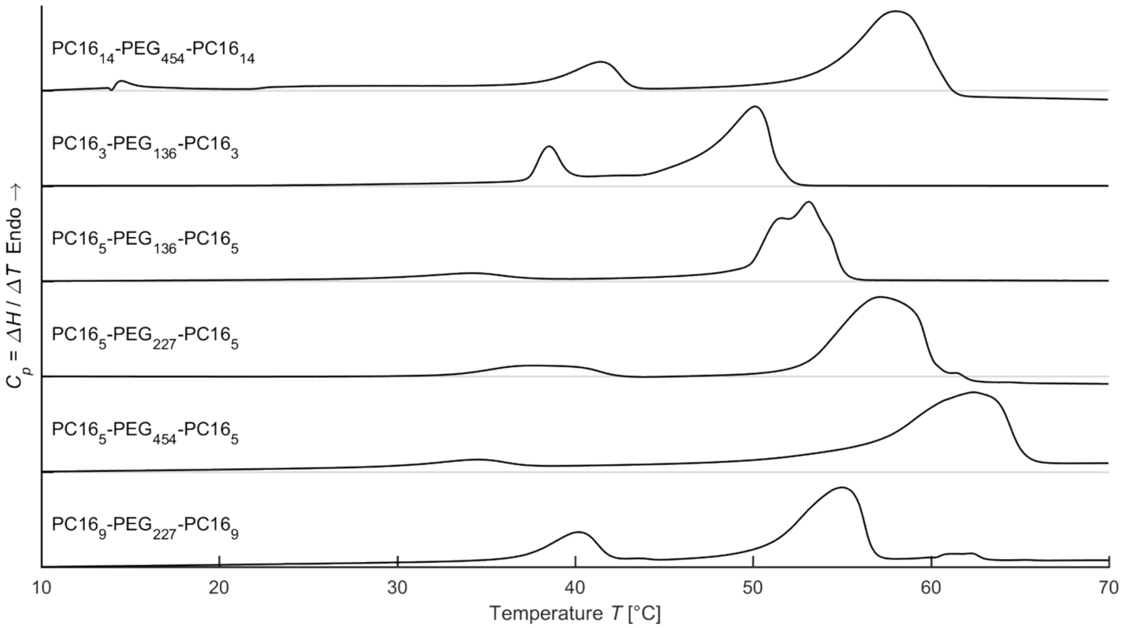

Figure S22. DSC-measurements of triblock copolymers containing PC16-AlkGE-blocks (in bulk).

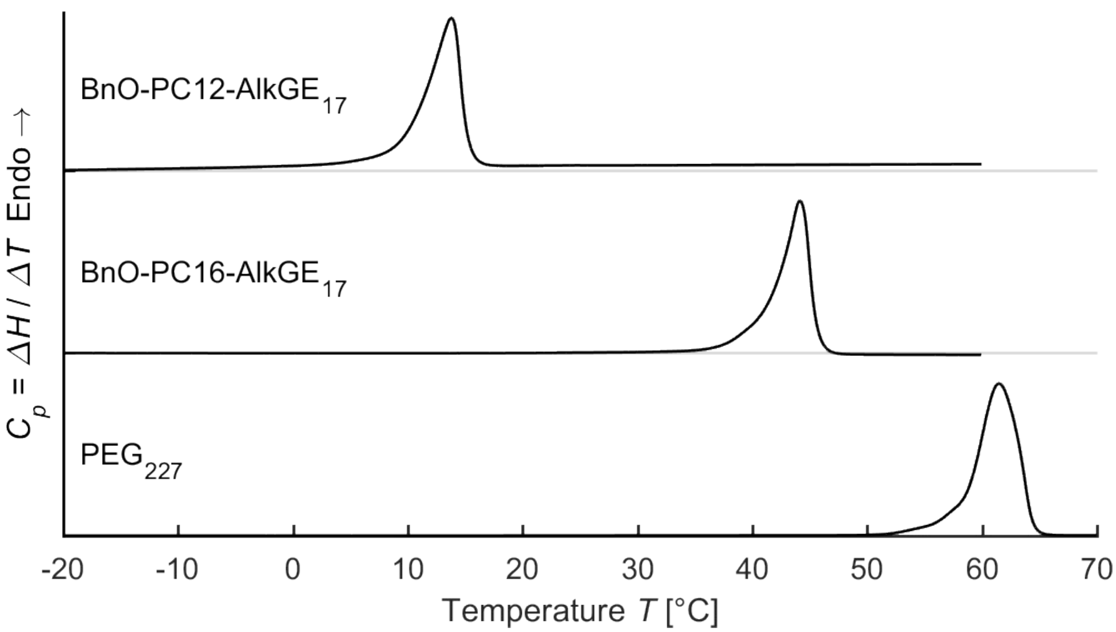

Figure S23. DSC-measurements of the homopolymers BnO-PC12-AlkGE$_{17}$, BnO-PC16-AlkGE$_{17}$ and PEG$_{227}$ as a reference (in bulk).

Table S2. Melting temperatures of the triblock copolymers in bulk.

Polymer sample	T_m[a] / °C in bulk	ΔH_m / J/g
$PC12_3$-*b*-PEG_{136}-*b*-$PC12_3$	0 / 53	6.4 / 111.4
$PC12_5$-*b*-PEG_{136}-*b*-$PC12_5$	8 / 52	16.2 / 84.8
$PC12_5$-*b*-PEG_{227}-*b*-$PC12_5$	2 / 57	9.5 / 113.2
$PC12_8$-*b*-PEG_{227}-*b*-$PC12_8$	10 / 56	14.1 / 88.2
$PC12_6$-*b*-PEG_{454}-*b*-$PC12_6$	0 / 61	3.1 / 113.2
$PC12_{12}$-*b*-PEG_{454}-*b*-$PC12_{12}$	11 / 61	8.3 / 98.9
$PC16_3$-*b*-PEG_{136}-*b*-$PC16_3$	33 / 52	10.6 / 100.9
$PC16_5$-*b*-PEG_{136}-*b*-$PC16_5$	38 / 50	11.9 / 67.1
$PC16_5$-*b*-PEG_{227}-*b*-$PC16_5$	37 / 52	14.8 / 91.5
$PC16_9$-*b*-PEG_{227}-*b*-$PC16_9$	40 / 54	22.5 / 78.9
$PC16_5$-*b*-PEG_{454}-*b*-$PC16_5$	34 / 62	7.7 / 113.9
$PC16_{14}$-*b*-PEG_{454}-*b*-$PC16_{14}$	41 / 57	16.0 / 79.8

[a] First melting temperature can be assigned to the hydrophobic AlkGE-block, second melting temperature is due to the hydrophilic PEG-block.

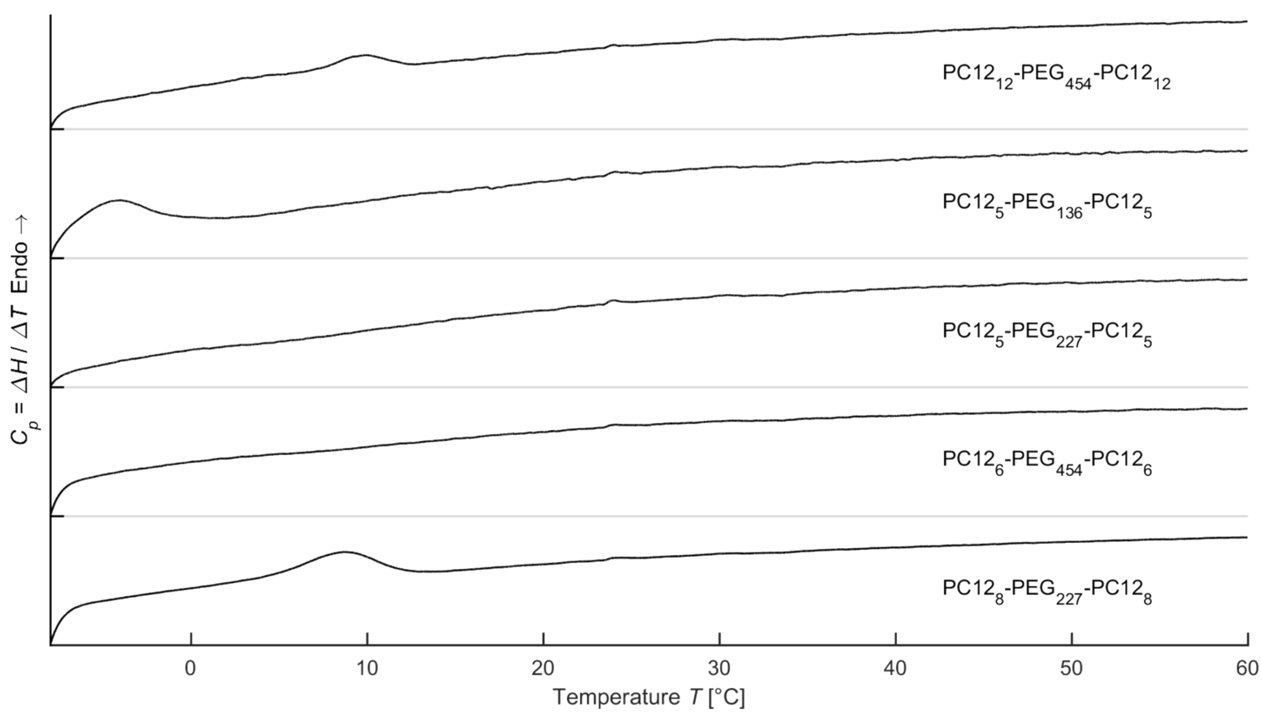

Figure S24. DSC-measurements of triblock copolymers containing PC12-AlkGE blocks in ethanol/water gels (at equilibrium swelling).

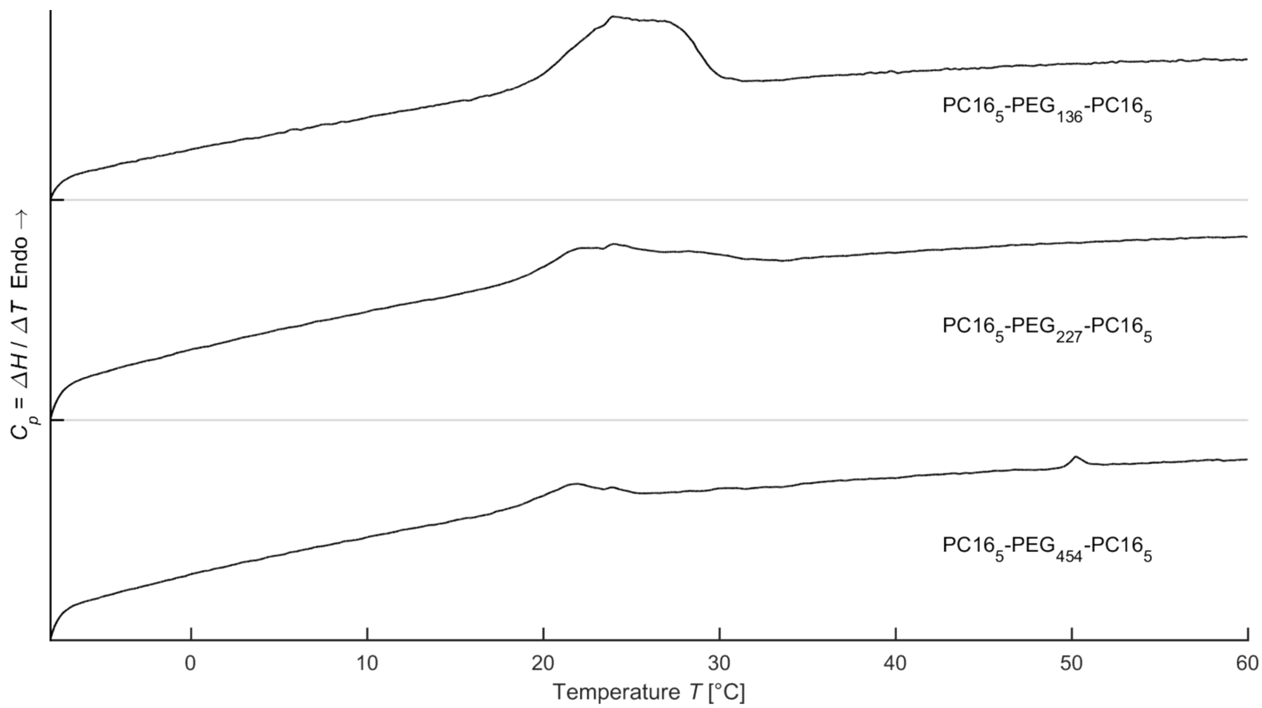

Figure S25. DSC-measurements of triblock copolymers containing PC16-AlkGE in ethanol/water gels (equilibrium swelling).

Table S3. Melting temperatures of the triblock copolymers in water/ethanol gels.

Polymer sample	**T_m / °C in water/ethanol gel**	**ΔH_m / J/g**
PC12$_3$-*b*-PEG$_{136}$-*b*-PC12$_3$	-	-
PC12$_5$-*b*-PEG$_{136}$-*b*-PC12$_5$	-5	0.5
PC12$_5$-*b*-PEG$_{227}$-*b*-PC12$_5$	- *	-
PC12$_8$-*b*-PEG$_{227}$-*b*-PC12$_8$	8	0.9
PC12$_6$-*b*-PEG$_{454}$-*b*-PC12$_6$	- *	-
PC12$_{12}$-*b*-PEG$_{454}$-*b*-PC12$_{12}$	9	0.3
PC16$_3$-*b*-PEG$_{136}$-*b*-PC16$_3$	-	-
PC16$_5$-*b*-PEG$_{136}$-*b*-PC16$_5$	23	2.8
PC16$_5$-*b*-PEG$_{227}$-*b*-PC16$_5$	23	0.8
PC16$_9$-*b*-PEG$_{227}$-*b*-PC16$_9$	-	-
PC16$_5$-*b*-PEG$_{454}$-*b*-PC16$_5$	21	0.3
PC16$_{14}$-*b*-PEG$_{454}$-*b*-PC16$_{14}$	-	-

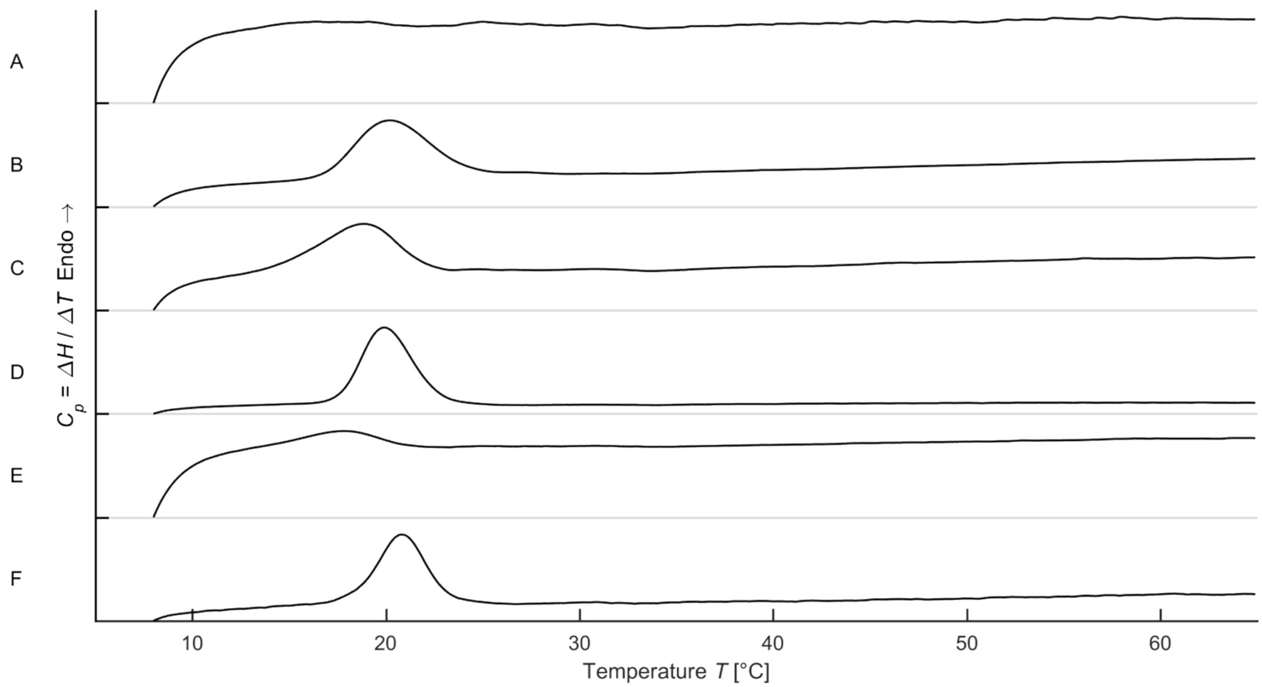

Figure S26. DSC-measurements of triblock copolymers containing PC12-AlkGE swollen in pure water. A: $PC12_3$-*b*-PEG_{136}-*b*-$PC12_3$, B: $PC12_5$-*b*-PEG_{136}-*b*-$PC12_5$, C: $PC12_6$-*b*-PEG_{227}-*b*-$PC12_6$, D: $PC12_8$-*b*-PEG_{227}-*b*-$PC12_8$, E: $PC12_6$-*b*-PEG_{454}-*b*-$PC12_6$, F: $PC12_{12}$-*b*-PEG_{454}-*b*-$PC12_{12}$.

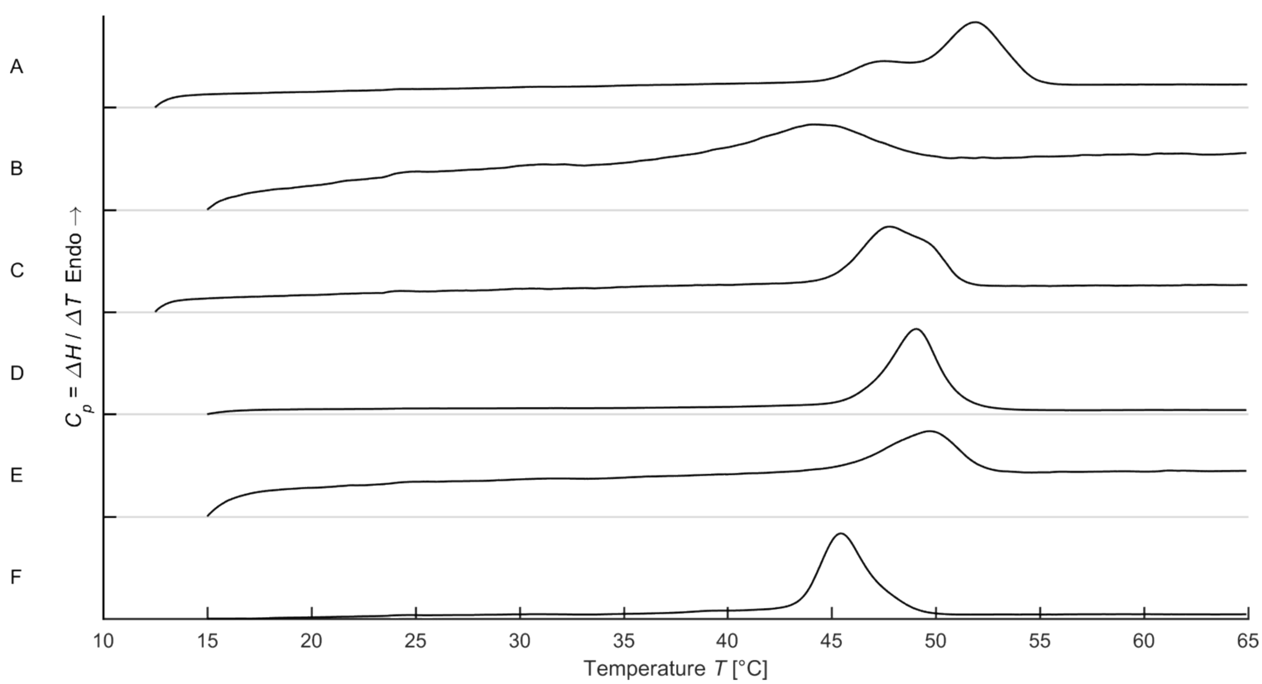

Figure S27. DSC-measurements of triblock copolymers containing PC16-AlkGE swollen in pure water. A: $PC16_3$-*b*-PEG_{136}-*b*-$PC16_3$, B: $PC16_5$-*b*-PEG_{136}-*b*-$PC16_5$, C: $PC16_5$-*b*-PEG_{227}-*b*-$PC16_5$, D: $PC16_9$-*b*-PEG_{227}-*b*-$PC16_9$, E: $PC16_5$-*b*-PEG_{454}-*b*-$PC16_5$, F: $PC16_{14}$-*b*-PEG_{454}-*b*-$PC16_{14}$.

Table S4. Melting temperatures of the triblock copolymers in hydrogels (no co-solvent present)

Polymer sample	T_m / °C in pure water	ΔH_m / J/g
$PC12_3$-*b*-PEG_{136}-*b*-$PC12_3$	-	-
$PC12_5$-*b*-PEG_{136}-*b*-$PC12_5$	19	2.5
$PC12_5$-*b*-PEG_{227}-*b*-$PC12_5$	18	0.9
$PC12_8$-*b*-PEG_{227}-*b*-$PC12_8$	19	3.6
$PC12_6$-*b*-PEG_{454}-*b*-$PC12_6$	17	0.5
$PC12_{12}$-*b*-PEG_{454}-*b*-$PC12_{12}$	20	1.6
$PC16_3$-*b*-PEG_{136}-*b*-$PC16_3$	43	0.6
$PC16_5$-*b*-PEG_{136}-*b*-$PC16_5$	47	5.9
$PC16_5$-*b*-PEG_{227}-*b*-$PC16_5$	47	2.9
$PC16_9$-*b*-PEG_{227}-*b*-$PC16_9$	48	7.9
$PC16_5$-*b*-PEG_{454}-*b*-$PC16_5$	49	0.9
$PC16_{14}$-*b*-PEG_{454}-*b*-$PC16_{14}$	44	4.1

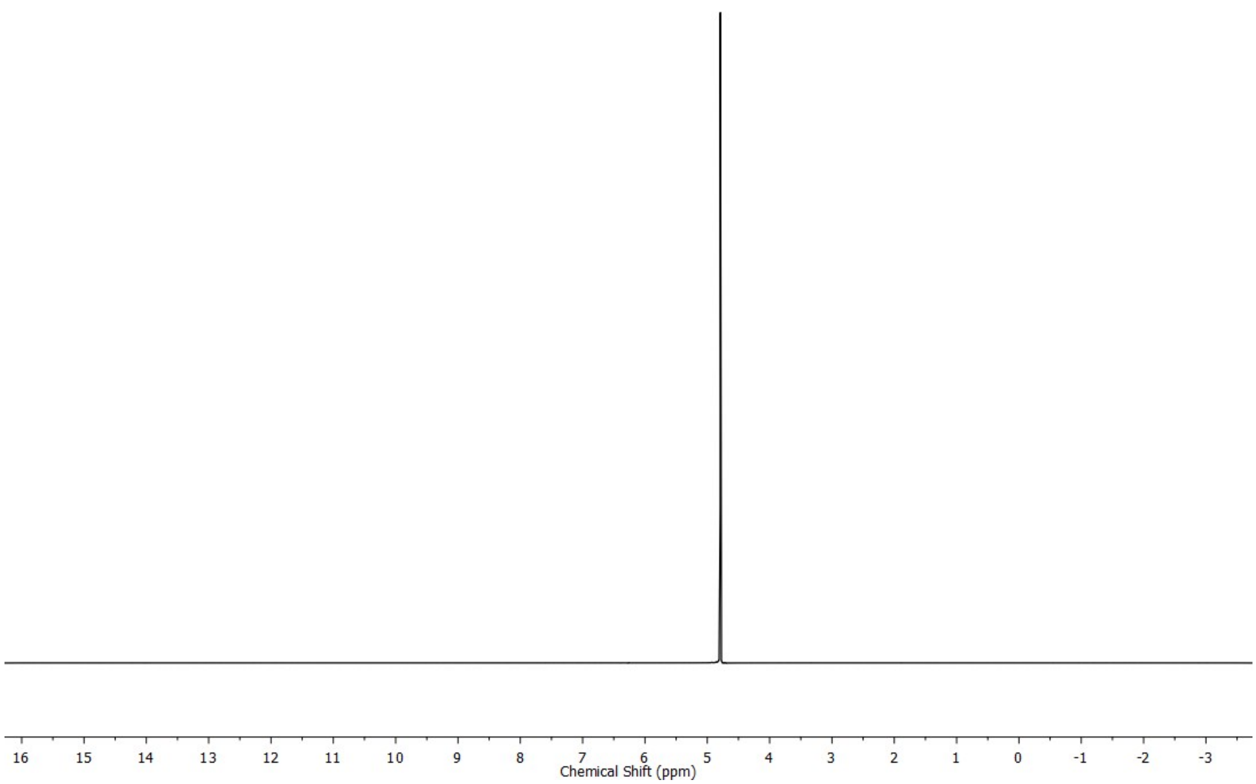

Figure S28. ^1H NMR spectrum (300 MHz, D_2O) of D_2O after the extraction of a loaded hydrogel sample to verify that there are no remainders of THF in the hydrogel after dialysis.

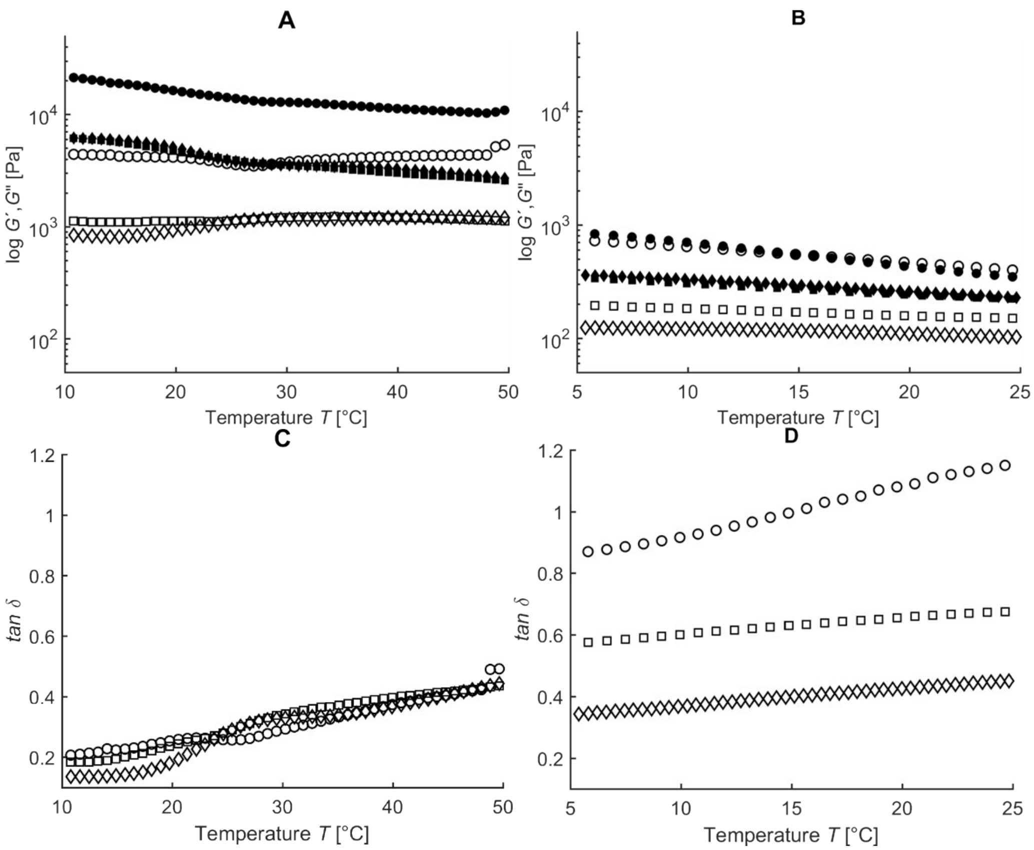

Figure S29. DMA analysis of the ethanol/water gels. A: PC16$_5$-*b*-PEG$_{136}$-*b*-PC16$_5$ (○), PC16$_5$-*b*-PEG$_{227}$-*b*-PC16$_5$ (□), PC16$_5$-*b*-PEG$_{454}$-*b*-PC16$_5$ (◊), G′, filled symbols; G′′, open symbols. B: PC12$_5$-*b*-PEG$_{136}$-*b*-PC12$_5$ (○), PC12$_6$-*b*-PEG$_{227}$-*b*-PC12$_6$ (□), PC12$_6$-*b*-PEG$_{454}$-*b*-PC12$_6$ (◊), G′, filled symbols; G′′, open symbols. C: loss factor tan δ as function of the temperature calculated from the data in A of PC16$_5$-*b*-PEG$_{136}$-*b*-PC16$_5$ (○), PC16$_5$-*b*-PEG$_{227}$-*b*-PC16$_5$ (□), PC16$_5$-*b*-PEG$_{454}$-*b*-PC16$_5$ (◊).D: loss factor tan δ as function of the temperature calculated from the data in B of PC12$_5$-*b*-PEG$_{136}$-*b*-PC12$_5$ (○), PC12$_6$-*b*-PEG$_{227}$-*b*-PC12$_6$ (□), PC12$_6$-*b*-PEG$_{454}$-*b*-PC12$_6$ (◊).

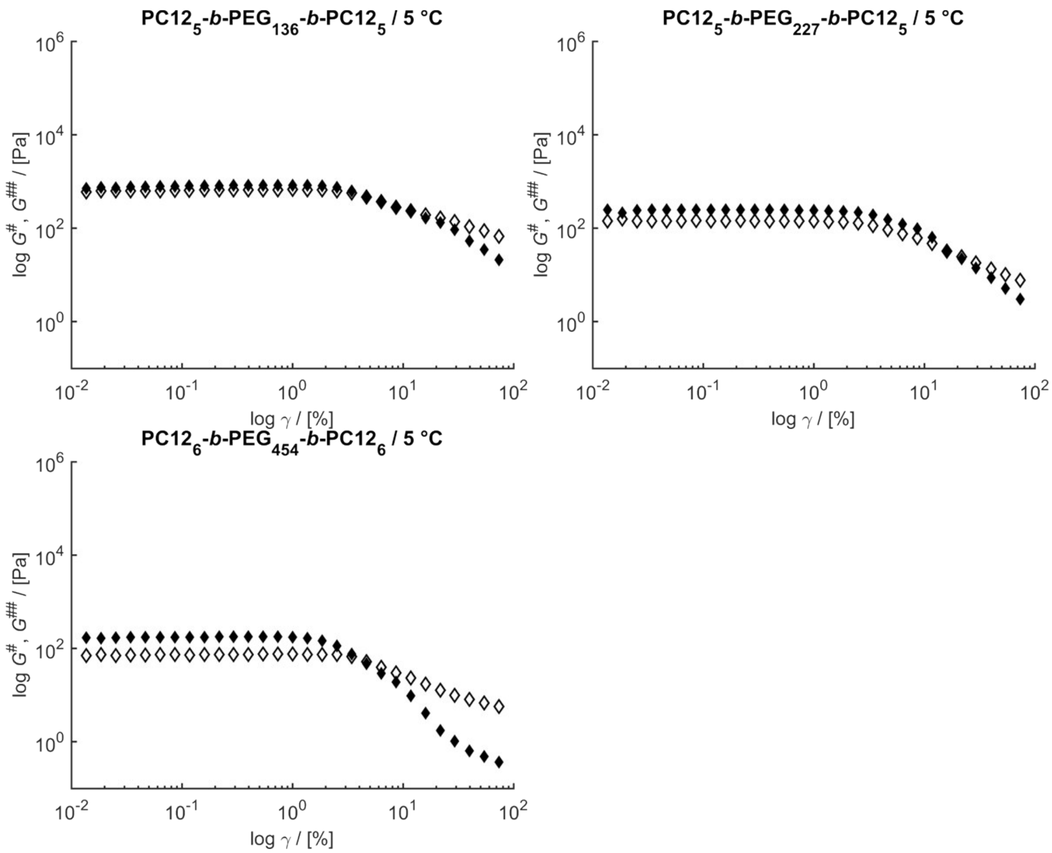

Figure S30. Amplitude sweep measurements of the ethanol/water gels containing PC12-AlkGE as a hydrophobic block and PEG (6k, 10k, 20k g mol^{-1}) as the central block at 5 °C.

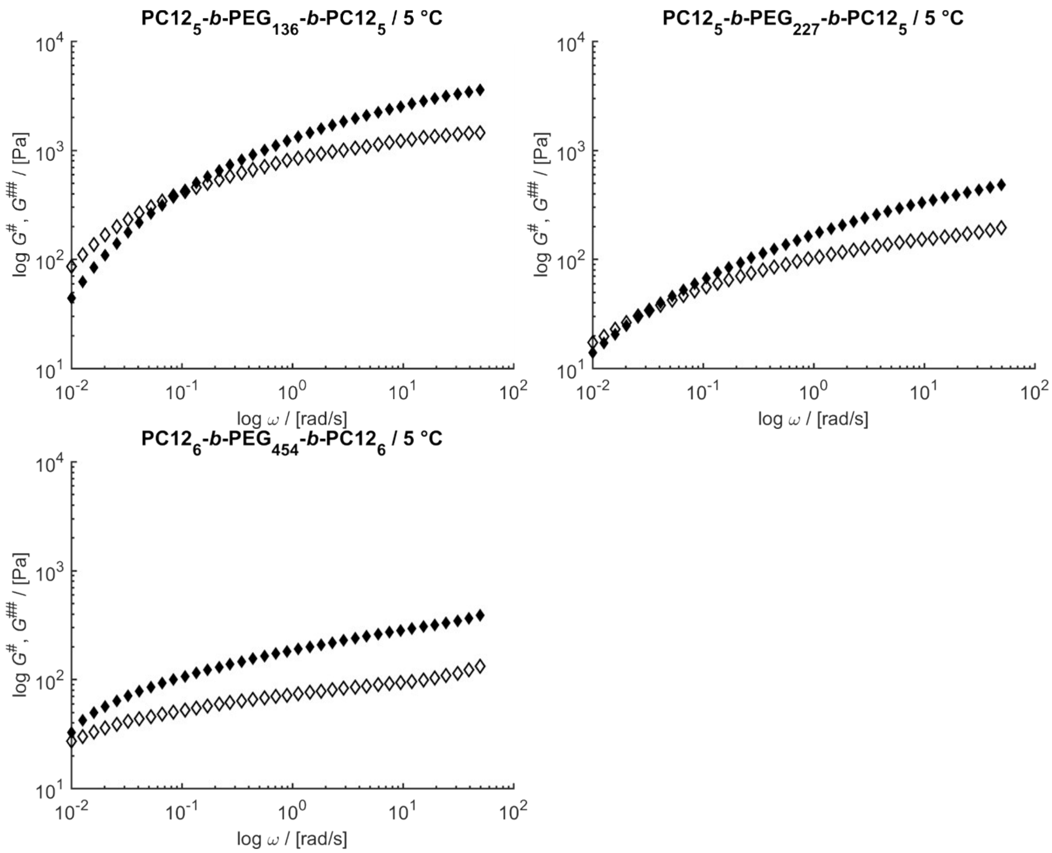

Figure S31. Frequency sweep measurements of the ethanol/water gels containing PC12-AlkGE as hydrophobic block and PEG (6k, 10k, 20k g mol^{-1}) as middle block at 5 °C.

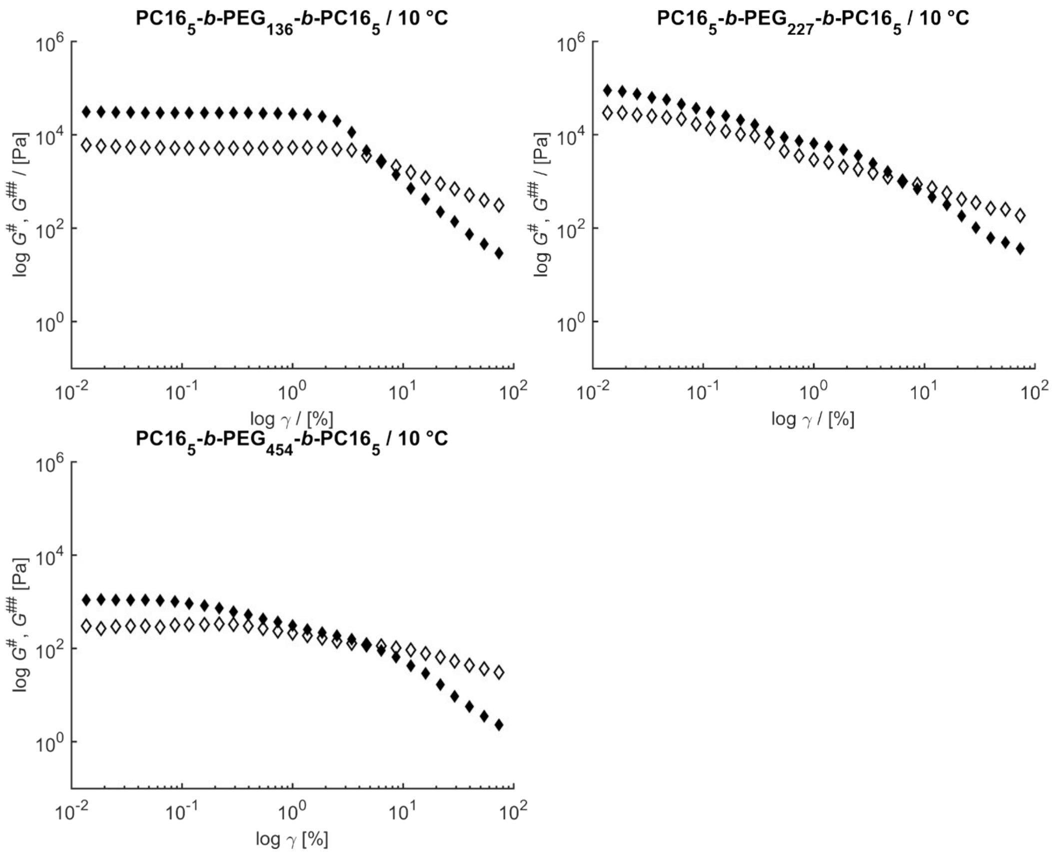

Figure S32. Amplitude sweep measurements of the ethanol/water gels containing PC16-AlkGE as hydrophobic block and PEG (6k, 10k, 20k g mol^{-1}) as middle block at 10 °C.

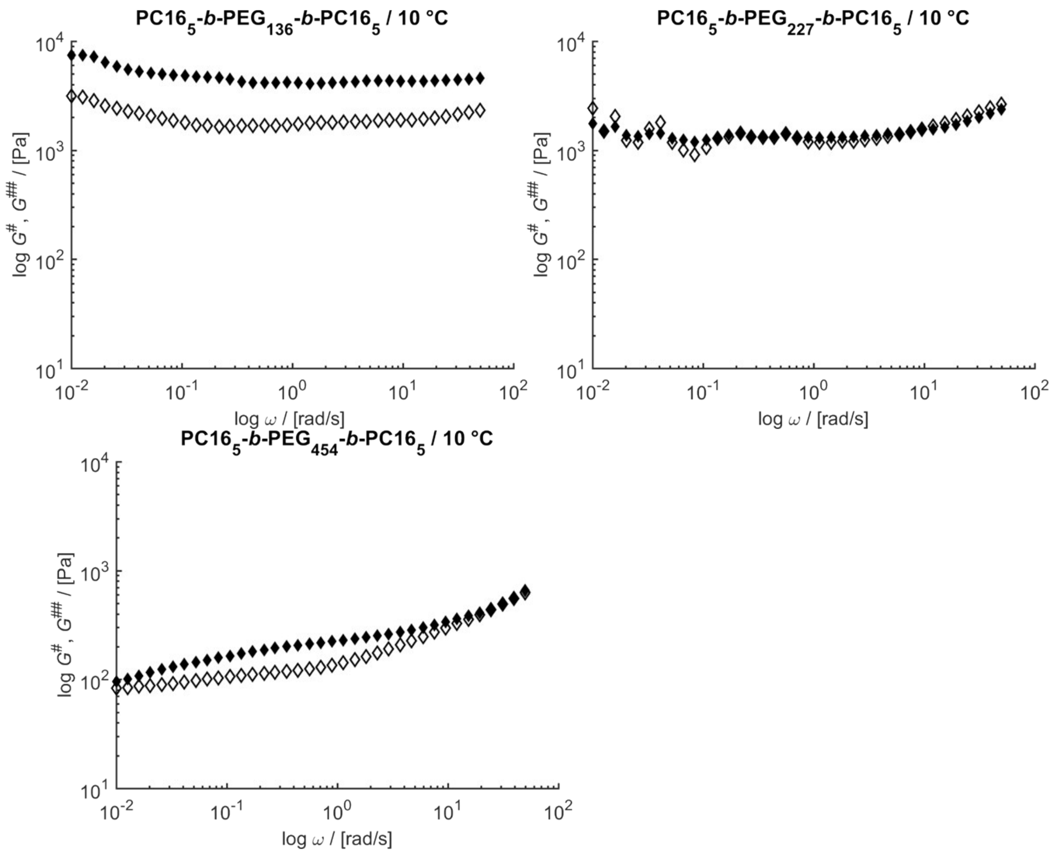

Figure S33. Frequency sweep measurements of the ethanol/water gels containing PC16-AlkGE as hydrophobic block and PEG (6k, 10k, 20k g mol^{-1}) as middle block at 10 °C.

References

1 a) S.-Y. Wu, A. Hirashima, R. Takeya and M. Eto, *Agricol. Biol. Chem.*, 1988, **52**, 2911–2917; b) L. F. Tietze and T. Eicher, *Reaktionen und Synthesen im organisch-chemischen Praktikum und Forschungslaboratorium*, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, FRG, 1991;