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Supporting Information

Blending of Reactive Prepolymers to Control the Morphology and Polarity of Polyglycidol-Based Microgels

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Experimental

Proton HRMAS transverse magnetization relaxation (T_2) NMR. The high-resolution MAS transverse relaxation (T_2) NMR measurements[1] were made at 700.2378 MHz proton frequency of Bruker AV700 NMR spectrometer. For these measurements ca. 5 wt % of the series of microgels dissolvend in deuterated water was used. The same rotor frequency, recycle delay, dwell time, and temperature as for ^{1}H HRMAS spectra were employed. The decay of transverse magnetization relaxation was measured using spin-echo pulse sequence: $90°_x$ - τ - $180°_{x,y}$ – τ- Hahn echo – (acquisition), where 2τ is the echo time. Half of the Hahn echo decay was detected and Fourier transformed. The normalized integral intensity of various peaks in the NMR spectrum was fitted by one- and two-exponential decay functions using Origin 6.0 software. The best-fit function was based on the χ^2 value. The errors of the fit parameters were smaller than 10 %.

Results and Discussion

Design of pro-hydrophilic and hydrophobic building blocks

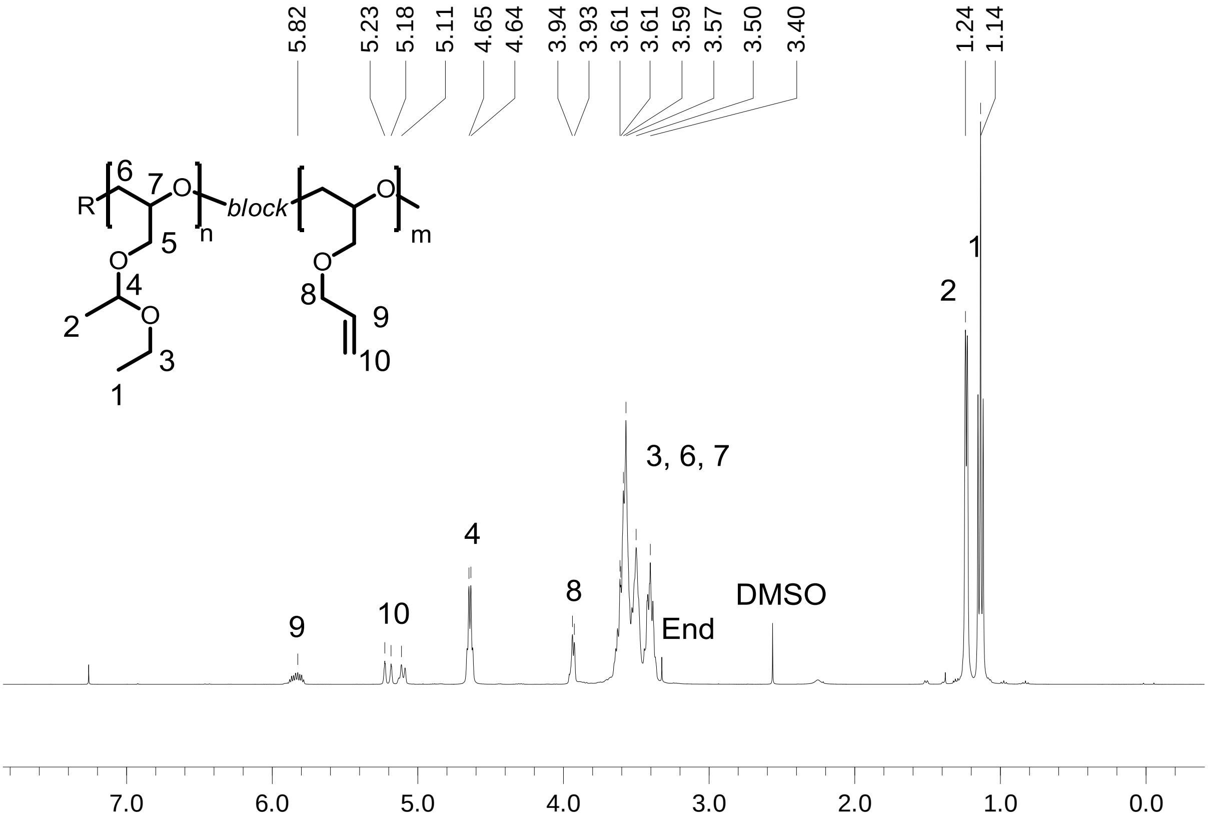


Figure SI 1. ^{1}H NMR spectrum of poly(EEGE)-*block*-poly(AGE), molar ratio EEGE/AGE = 4:1 (prepolymer **I**).

The signals 1, 2 and 4 confirm that the ethoxy ethyl acetal protecting group is stable under the polymerization conditions. The signals 8, 9 and 10 prove the stability of the allyl group. Additionally, Figure SI 2 shows the corresponding SEC and MALDI TOF MS data for the same prepolymer (EEGE/AGE, molar ratio 4:1, prepolymer **I**), which confirms the formation of a block copolymer since the retention volume is shifted to lower values after addition of the second monomer. Moreover, a signal for pure homopolymer is absent in the corresponding

MALDI TOF spectrum, which proves quantitative block extension. However, a more detailed, quantitative interpretation of the MALDI TOF MS data is difficult, since the baseline is not smooth.

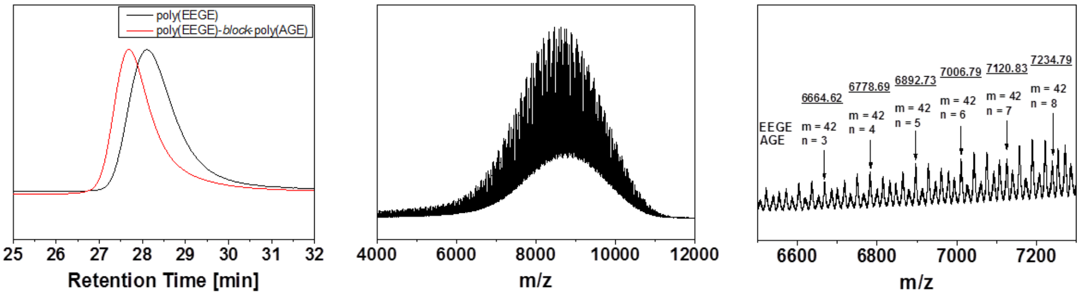
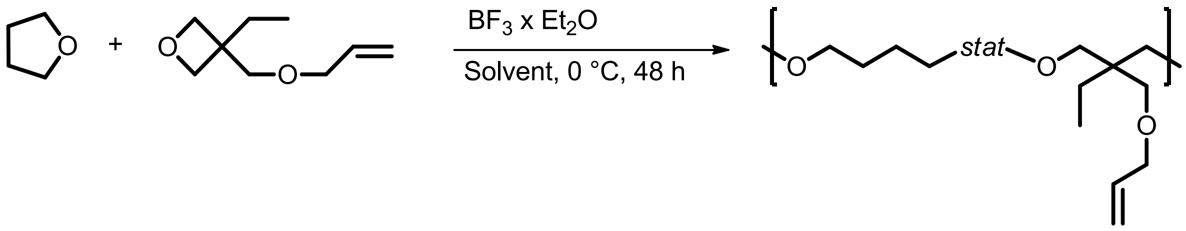


Figure SI 2. SEC traces of poly(EEGE) (black) as first block and poly(EEGE)-*block*-poly(AGE) (red), molar ratio EEGE : AGE = 4 : 1 (prepolymer **I**), and corresponding MALDI TOF MS data.

Synthesis of the hydrophobic prepolymer poly(THF-stat-AllylEHO)

We aim with our work at a modification of the morphology and the polarity of the microgel and that is why we decided to use a second, hydrophobic component, which we add to pro-hydrophilic poly(EEGE)-*block*-poly(AGE). We chose on the one hand a statistical copolymer of tetrahydrofuran (THF) and 3-allyloxymethyl-3-ethyloxetane (AllylEHO) repeating units and on the orther hand polystyrene homopolymer (M_n = 17500 g/mol, $Đ_M$ = 1.04) as possible candidates.. THF and AllylEHO are both hydrophobic building blocks, and AllylEHO adds chemical functionality to poly(THF). By careful choice of the initiator and the solvent for the cationic ring-opening polymerization (CROP), it is possible to obtain polymers with different ratios of AllylEHO and THF. BF_3 x Et_2O is an initiator for the polymerization of AllylEHO, however, it does not polymerize THF. Nevertheless, it is possible to synthesize a copolymer of THF and AllylEHO with BF_3 x Et_2O, as AllyEHO serves as promotor for the polymerization of THF. This means that due to the basicity of the oxetane group the polymerization starts by protonation of the oxetane moiety. Subsequently, the corresponding electrophilic oxonium ion is attacked by THF monomer. In our experiments, we used typical solvents for CROP: THF, nitromethane and dichloromethane. Table SI 1 summarizes the properties of poly(THF-*stat*-AllylEHO) with regard to the solvent used, the ratio of the comonomers in the feed, composition of the copolymers and molecular weight.

Table SI 1. Solvent, ratio of comonomers in the feed, composition of the copolymers, molecular weight and dispersity of poly(THF-*stat*-AllylEHO).



THF **AllylEHO** **poly(THF-*stat*-AllylEHO)**

Pre-polymer	Solvent for Synthesis	Molar Ratio of Comomers in the Feed (AllylEHO:THF)	Molar Ratio of Repeating Units in the Copolymer (AllylEHO:THF)	$M_{n(SEC, THF)}$ [g/mol]	$Đ_M$
II	THF	excess (solvent)	0.35:1	49200	2.38
III	CH_3NO_2	1:1	3.2:1	13400	2.79
IV	CH_2Cl_2	1:1	9.3:1	5200	1.70

The synthesis in dichloromethane and in nitromethane yields materials, in which the oxetane building block constitutes the major part of the final polymer (ratio AllylEHO:THF = 3.2:1 and 9.3:1, respectively), whereas the sample where THF served as solvent as well as comonomer contains more THF than AllylEHO (ratio AllylEHO:THF = 0.35:1). The dispersity of all three polymers is typical for a most probable distribution of molecular weights. Figure SI 3 shows a typical ^1H NMR spectrum of poly(THF-*stat*-AllylEHO) polymerized in THF, which proves by the presence of the signals 9, 10 and 11 that the allyl group is stable under the acidic conditions of CROP. The signals 2 and 4 are used to determine the ratio between AllylEHO and THF.

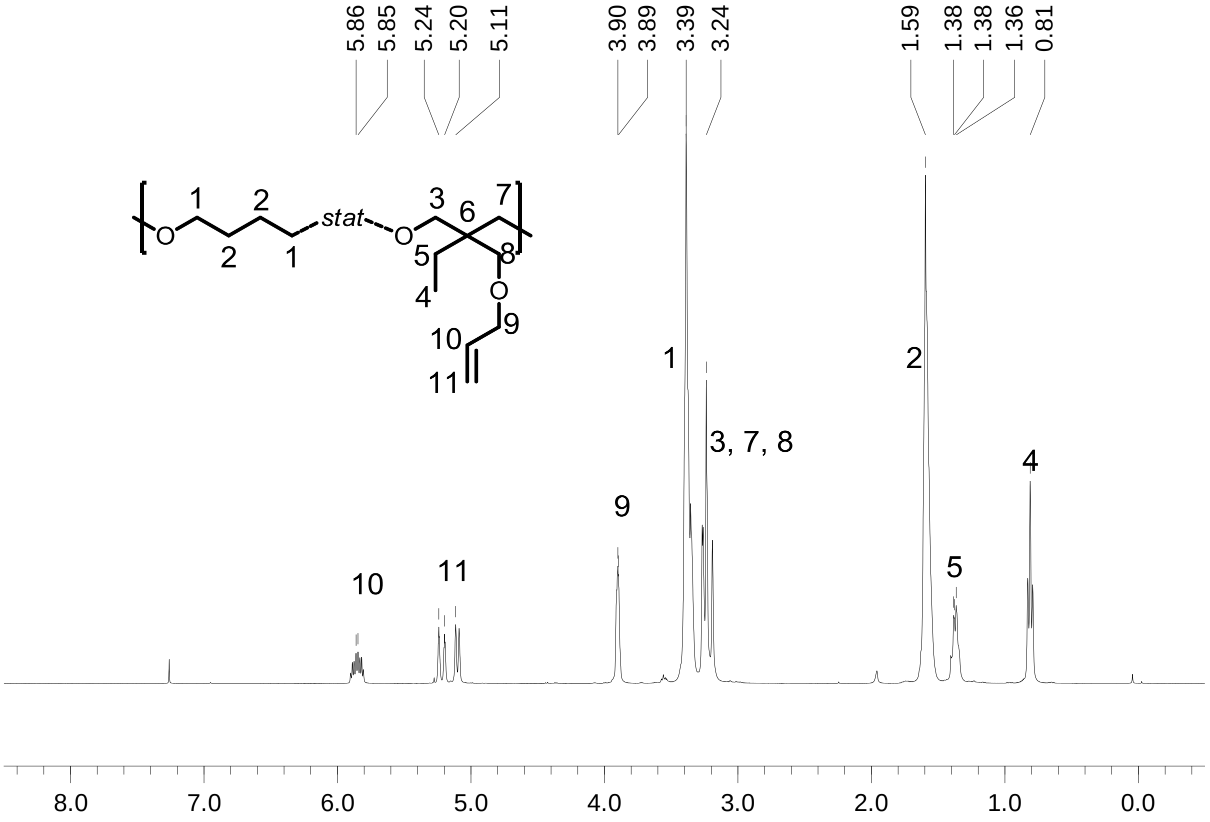


Figure SI 3. ^{1}H NMR spectrum of poly(THF-*stat*-AllylEHO) obtained in THF (prepolymer **II.**).

Microstructure of the hydrophobic prepolymer poly(THF-stat-AllylEHO)

Careful analysis of the ^{13}C NMR data for poly(THF-*stat*-AllylEHO) allows characterizing the microstructure through triad analysis. Apart from that it is possible to determine the average sequence length of THF and AllyEHO building blocks in the obtained copolymers. The composition of poly(THF-*stat*-AllylEHO) is highly dependent on the solvent used for synthesis. Whereas the synthesis in dichloromethane and nitromethane yields polymer where an excess of AllylEHO is incorporated, the synthesis in THF yield a polymer with an excess of THF. Accordingly, the careful choice of the solvent permits to adjust the composition of the statistical copolymer. ^{13}C NMR spectroscopy is a valuable tool for the description of the microstructure of polymers. For statistical copolymers the qualitative analysis of the chemical shift of the signals and the comparison with the respective chemical shift in the homopolymers allows describing triad sequence in the copolymer. Furthermore, a quantitative analysis leads to a description of sequence lengths. Figure SI 4 shows sections of the ^{13}C NMR spectrum between 69-75 ppm of poly(THF) (Figure SI 4 (a)) and poly(AllylEHO) (Figure SI 4 (b)). In poly(THF) the carbon atoms in the vicinity of the oxygen have a chemical shift of 70.6 ppm. Two dimensional NMR spectroscopy of poly(AllylEHO) shows that the carbon atoms adjacent to the oxygen atom in the polymer backbone have a chemical shift of 71.6 ppm. The carbon atoms adjacent to the oxygen atom in the side chains have a chemical shift of 71.2 (allyl position) and of 72.3 ppm (methylene-oxy group).

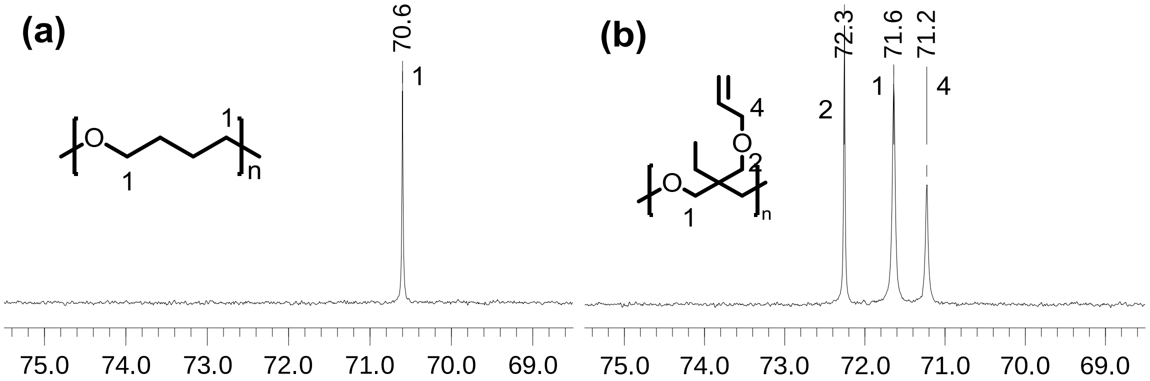


Figure SI 4. ^{13}C NMR spectra of poly(THF) (a) and poly(AllylEHO) (b) homopolymer.

Figure SI 5 shows sections of the ^{13}C NMR spectrum of the region between 69-75 ppm for poly(THF-*stat*-AllylEHO) prepolymers **II** – **IV** synthesized in THF, nitromethane and dichloromethane. Based on the knowledge of the ratio of the repeating units in the product from ^{1}H NMR spectroscopy and on the comparison of the chemical shift of the respective signals in the ^{13}C NMR spectrum for the pure homopolymers, we assign the following chemical shifts for the triads.

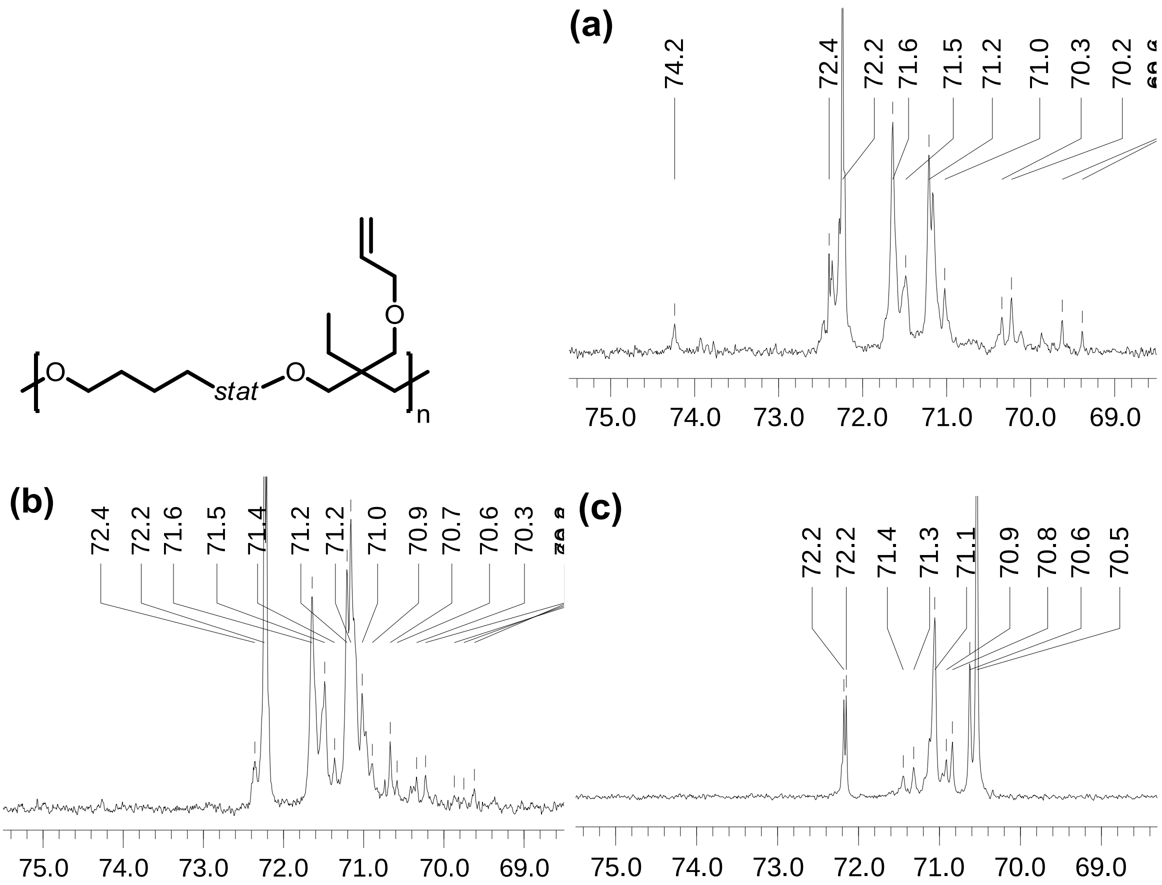


Figure SI 5. ^{13}C NMR spectra of poly(THF-*stat*-AllylEHO) synthesized in dichloromethane (a), nitromethane (b) and THF (c).

Poly(THF-*stat*-AllylEHO) synthesized in dichloromethane:

AllylEHO-**AllylEHO**-AllylEHO	71.6 ppm
THF-**AllylEHO**-AllylEHO	71.5 ppm
AllylEHO-**AllylEHO**-THF	71.5 ppm
THF-**AllylEHO**-THF	-
AllylEHO-**THF**-AllylEHO	69.4 – 69.6 ppm
THF-**THF**-AllylEHO	70.1 – 70.3 ppm
AllylEHO-**THF**-THF	70.1 – 70.3 ppm
THF-**THF**-THF	-

Poly(THF-*stat*-AllylEHO) synthesized in nitromethane:

AllylEHO-**AllylEHO**-AllylEHO	71.6 ppm
THF-**AllylEHO**-AllylEHO	71.5 ppm
AllylEHO-**AllylEHO**-THF	71.5 ppm
THF-**AllylEHO**-THF	71.4 ppm

AllylEHO-**THF**-AllylEHO	69.6 – 69.9 ppm
THF-**THF**-AllylEHO	70.2 – 70.4 ppm
AllylEHO-**THF**-THF	70.2 – 70.4 ppm
THF-**THF**-THF	70.6 – 70.7 ppm

Poly(THF-*stat*-AllylEHO) synthesized in tetrahydrofuran:

AllylEHO-**AllylEHO**-AllylEHO	-
THF-**AllylEHO**-AllylEHO	71.5 ppm
AllylEHO-**AllylEHO**-THF	71.5 ppm
THF-**AllylEHO**-THF	71.3 ppm

AllylEHO-**THF**-AllylEHO	-
THF-**THF**-AllylEHO	70.2 – 70.4 ppm
AllylEHO-**THF**-THF	70.2 – 70.4 ppm
THF-**THF**-THF	70.6 ppm

From the ratio of homo and hetero diads it is possible to estimate the average sequence length[2] according to

$$\bar{L}_{THF} = \frac{I_{THF/THF}}{I_{THF/AllylEHO}} + 1 = \frac{I_{THF/THF}}{I_{AllylEHO/THF}}$$

$$\bar{L}_{AllylEHO} = \frac{I_{AllylEHO/AllylEHO}}{I_{AllylEHO/THF}} + 1 = \frac{I_{THF/THF}}{I_{THF/AllylEHO}}$$

Poly(THF-*stat*-AllylEHO) synthesized in dichloromethane:

$\overline{L}_{AllylEHO}$ =5.26

Poly(THF-*stat*-AllylEHO) synthesized in nitromethane:

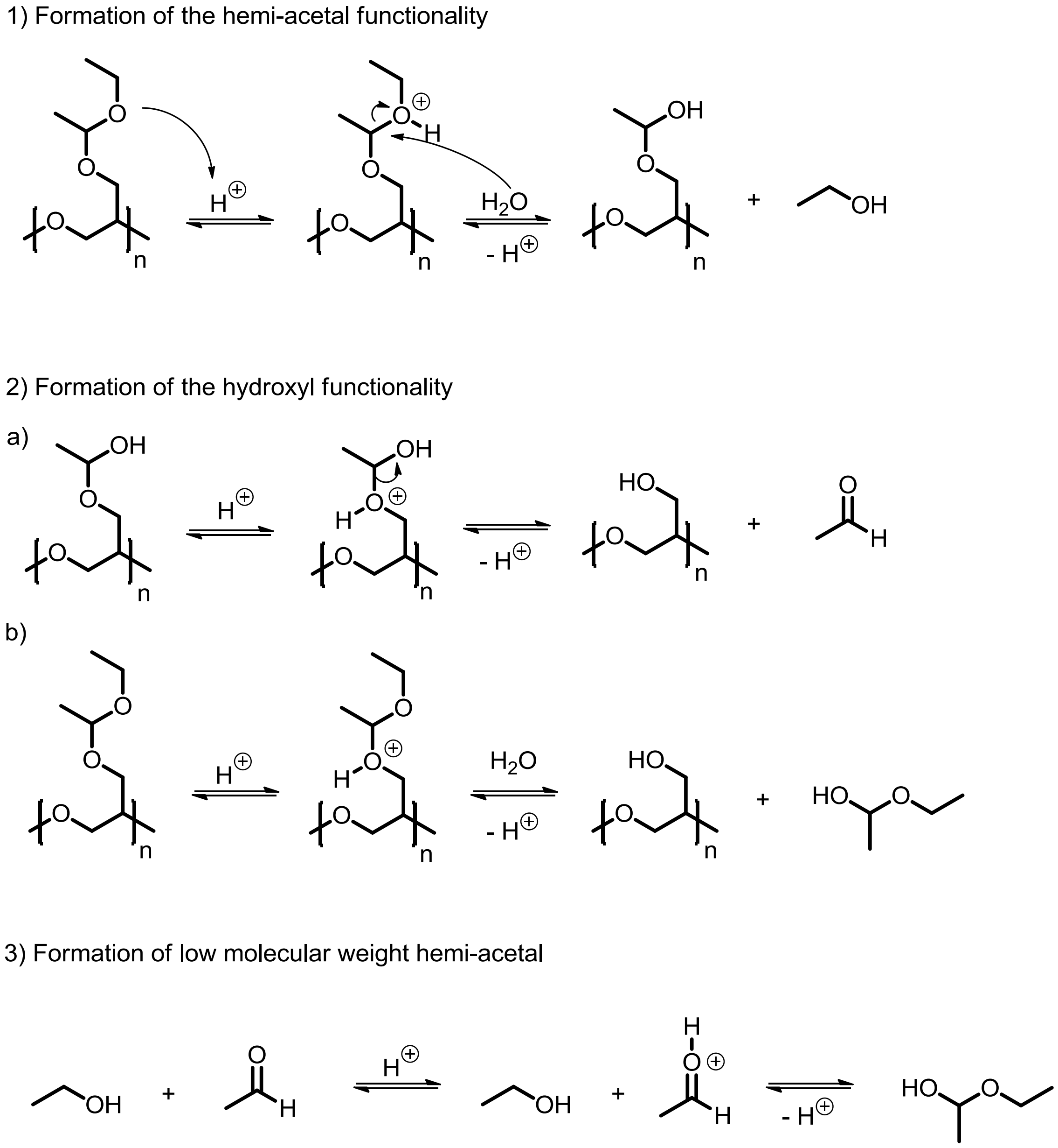
$\overline{L}_{THF} = 1.1$

$\overline{L}_{AllylEHO} = 2.7$

Poly(THF-*stat*-AllylEHO) synthesized in tetrahydrofuran:

$\overline{L}_{AllylEHO}$ =1.35

Mechanism of hydrolysis of ethoxy ethyl acetal group in poly(EEGE)



Scheme SI 1. Hydrolysis of the acetal group in poly(ethoxy ethyl glycidyl ether) (poly(EEGE)) by acidic hydrolysis.

Second set of ^{1}H NMR measurements 12 hours after sample preparation (compare with Fig. 2 in the main document).

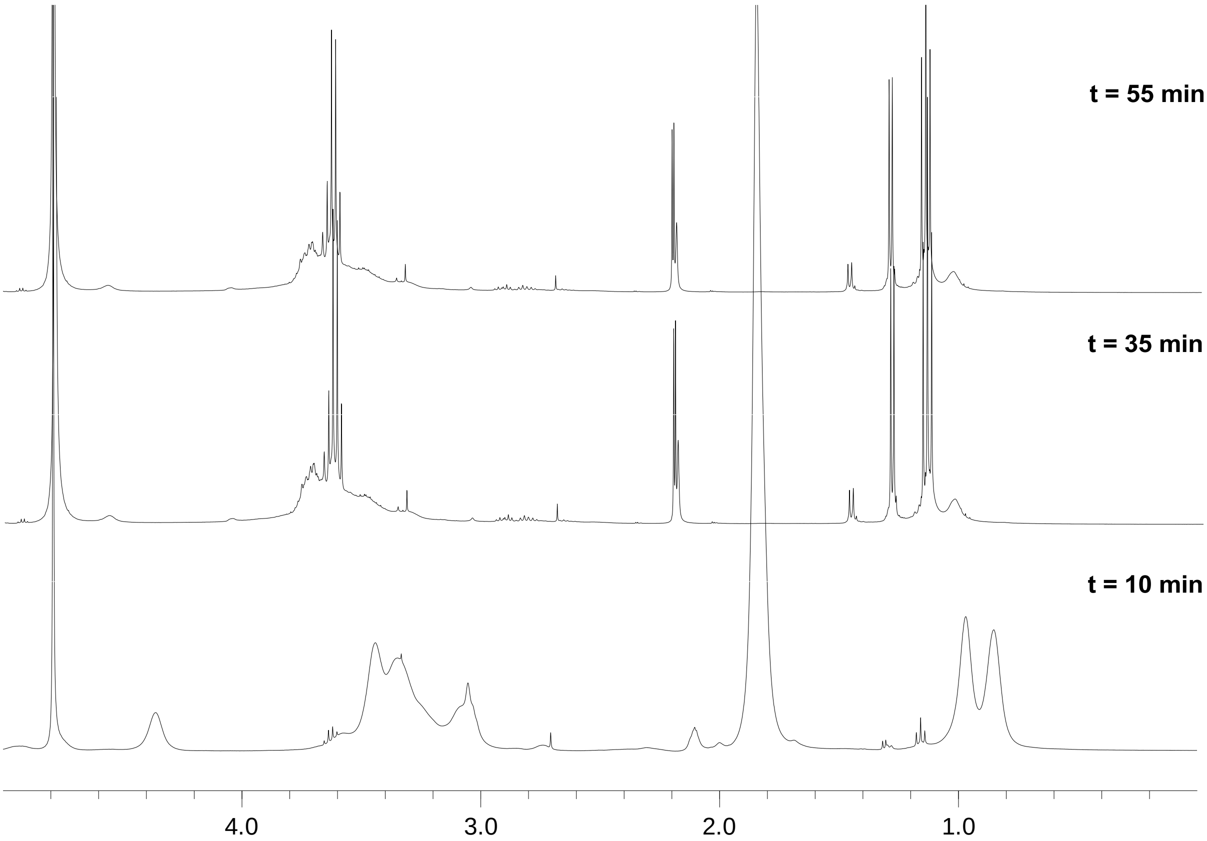


Figure SI 6. Comparison of ^{1}H NMR spectra of model crosslinking reaction of poly(EEGE)-*block*-poly(AGE) (prepolymer **VI**) with 2,2’-(ethylenedioxy)-diethanethiol in D_2O twelve hours after sample preparation.

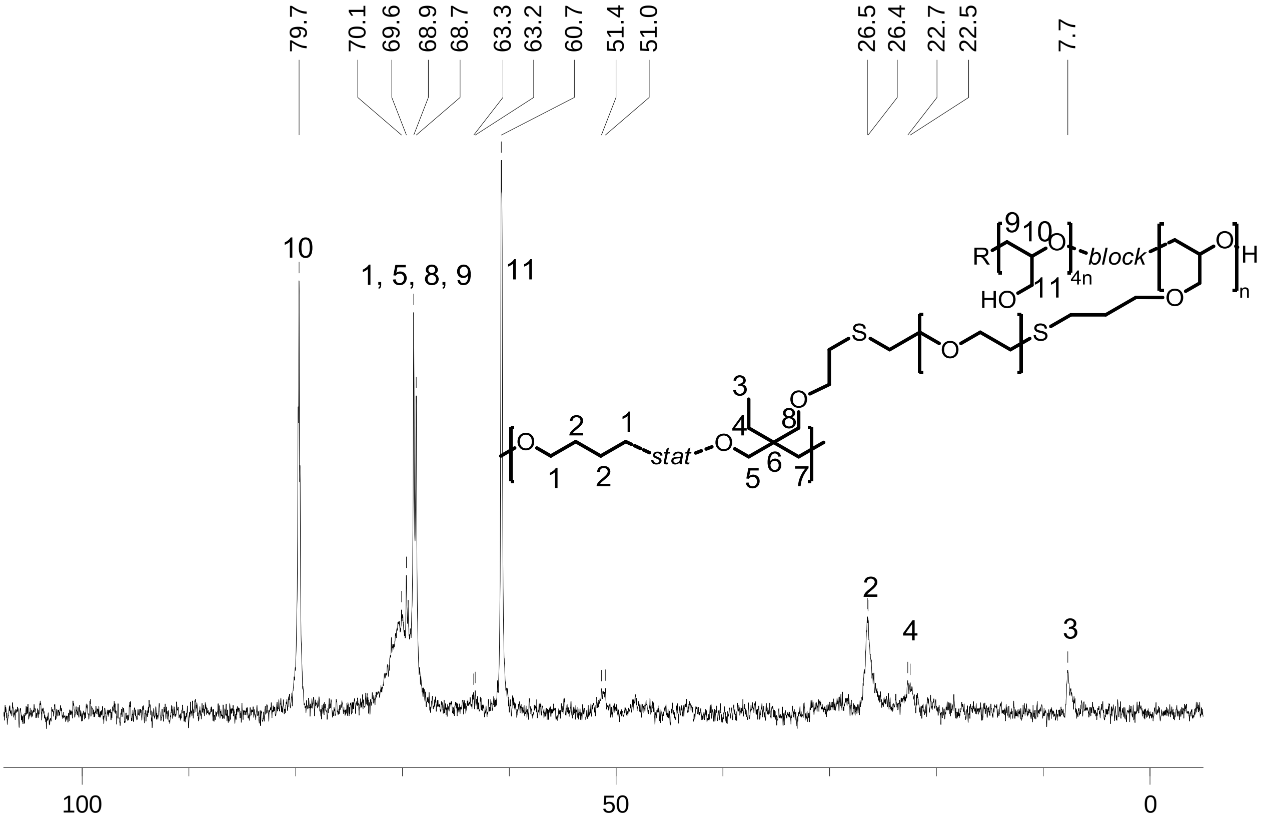


Figure SI 7. ^{13}C NMR spectrum of microgel **3** composed of 80 wt. % poly(EEGE)-*block*-poly(AGE) and 20 wt. % poly(THF-*stat*-AllylEHO).

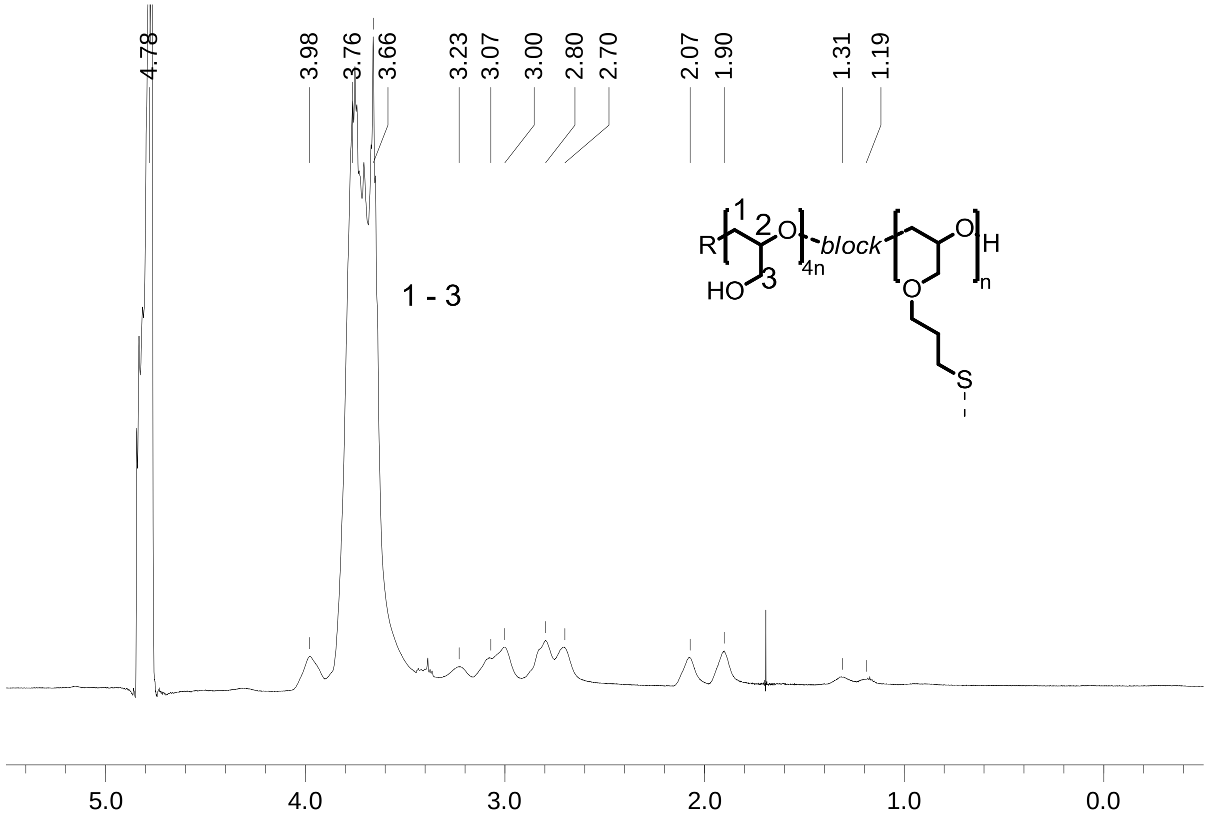


Figure SI 8. ^{1}H NMR spectrum of microgel composed purely of poly(EEGE)-*block*-poly(AGE).

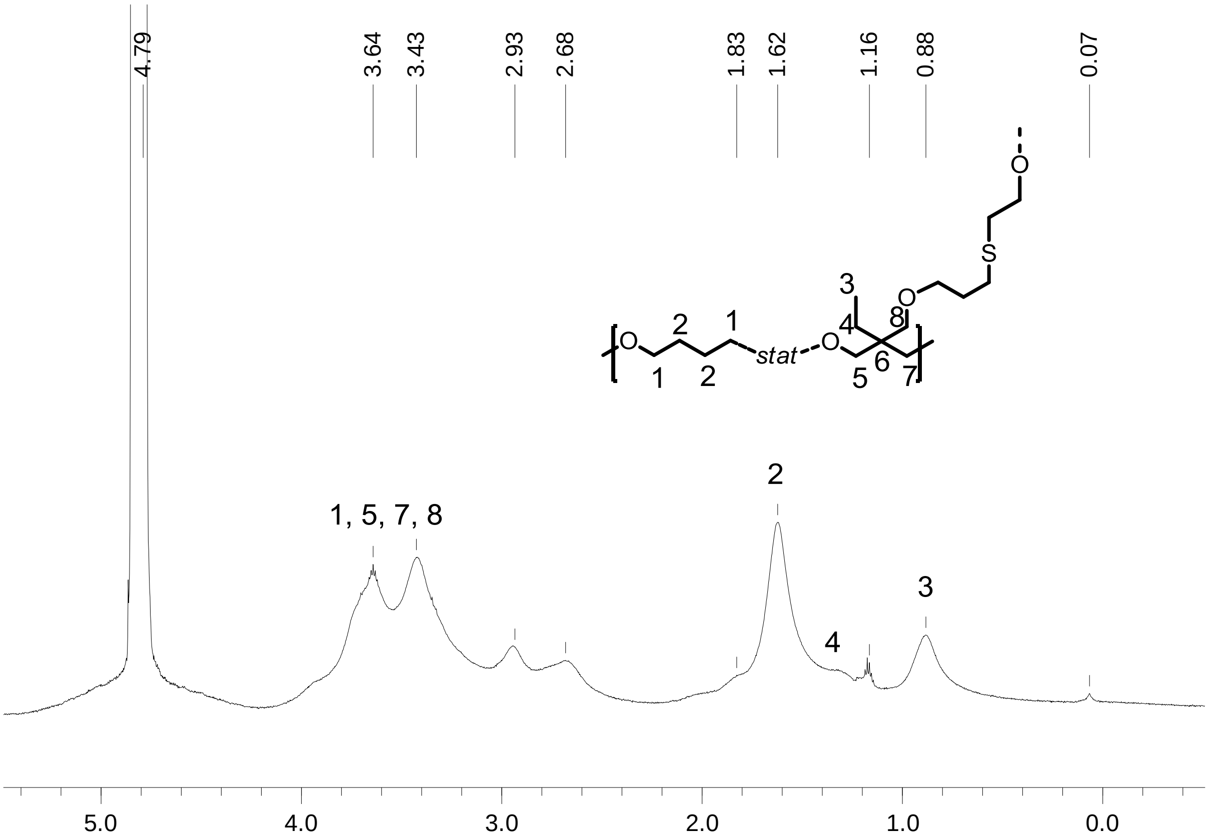


Figure SI 9. ^{1}H NMR spectrum of organogel composed purely of poly(THF-*stat*-AllylEHO).

Table SI 2. Transverse magnetization relaxation times T_2 in different microgel samples.

Micro-gel	Component	$T_{2,S}$ [ms]	$T_{2,L}$ [ms]	C_S	C_L	y_0	R^2 in fit	χ^2 in fit
1	hydrophil.	33	-	1.12577	-	-0.18811	0.99204	$5.367*10^{-4}$
3	hydrophil.	2	45	0.16947	1.14699	-0.3403	0.99413	$4.197*10^{-4}$
3	hydrophob.	0.6	11	0.39769	0.65743	-0.00348	0.98505	$9.493*10^{-4}$
9	hydrophob.	0.3	4	0.29873	0.80366	0.05439	0.98998	$7.980*10^{-4}$

References

1. Ernst, R. R.; Bodenhausen, G.; Wokaun, A., *Principles of Nuclear Magnetic Resonance in One and Two Dimensions*. Clarendon Press: Oxford, 1987.

2. Odelius, K.; Plikk, P.; Albertsson, A.-C. *Biomacromolecules* **2005**, *6*, 2718-2725.