Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting information

Responsive Microgels with Supramolecular Crosslinks: Synthesis and Triggered Degradation in Aqueous Medium

Dominik Schmitz, Andrij Pich

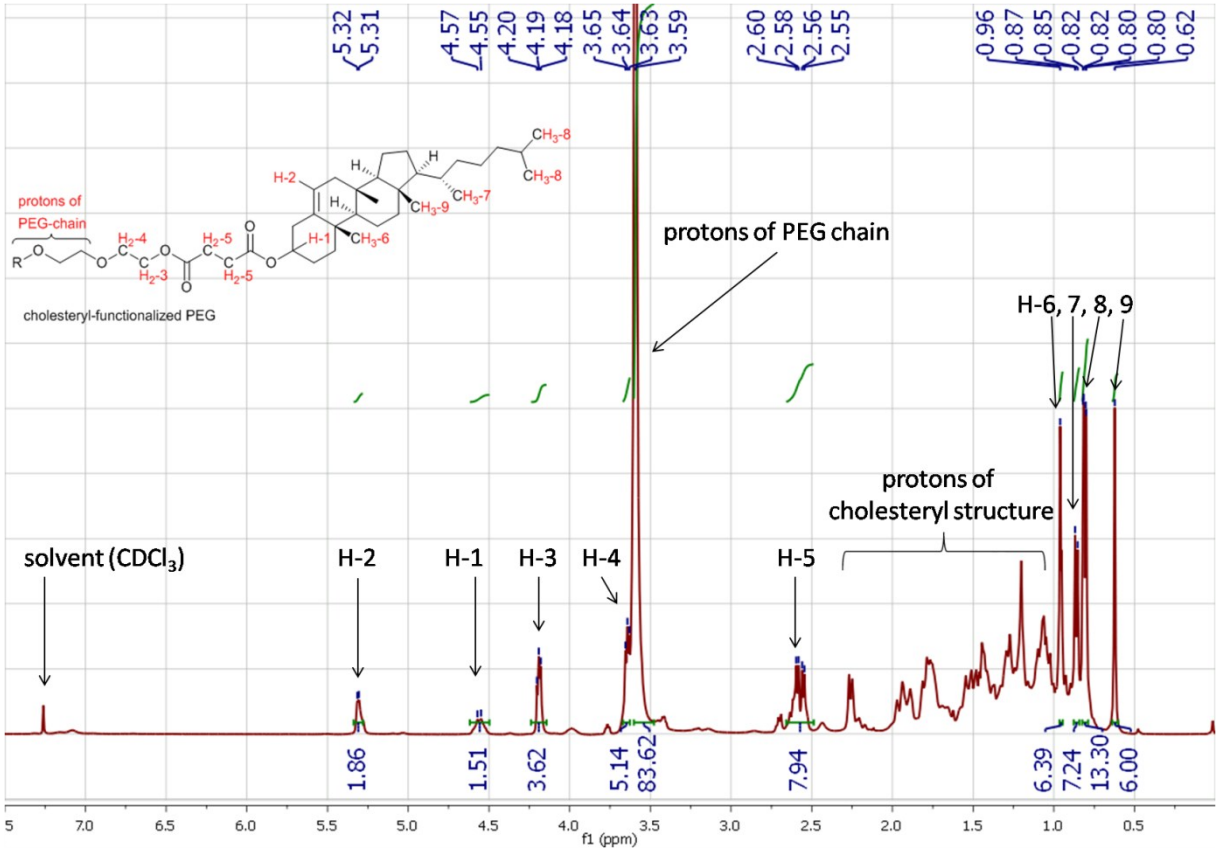


Fig. S1: ^{1}H-NMR spectrum of PEG1000-(chol.)$_2$ in $CDCl_3$.

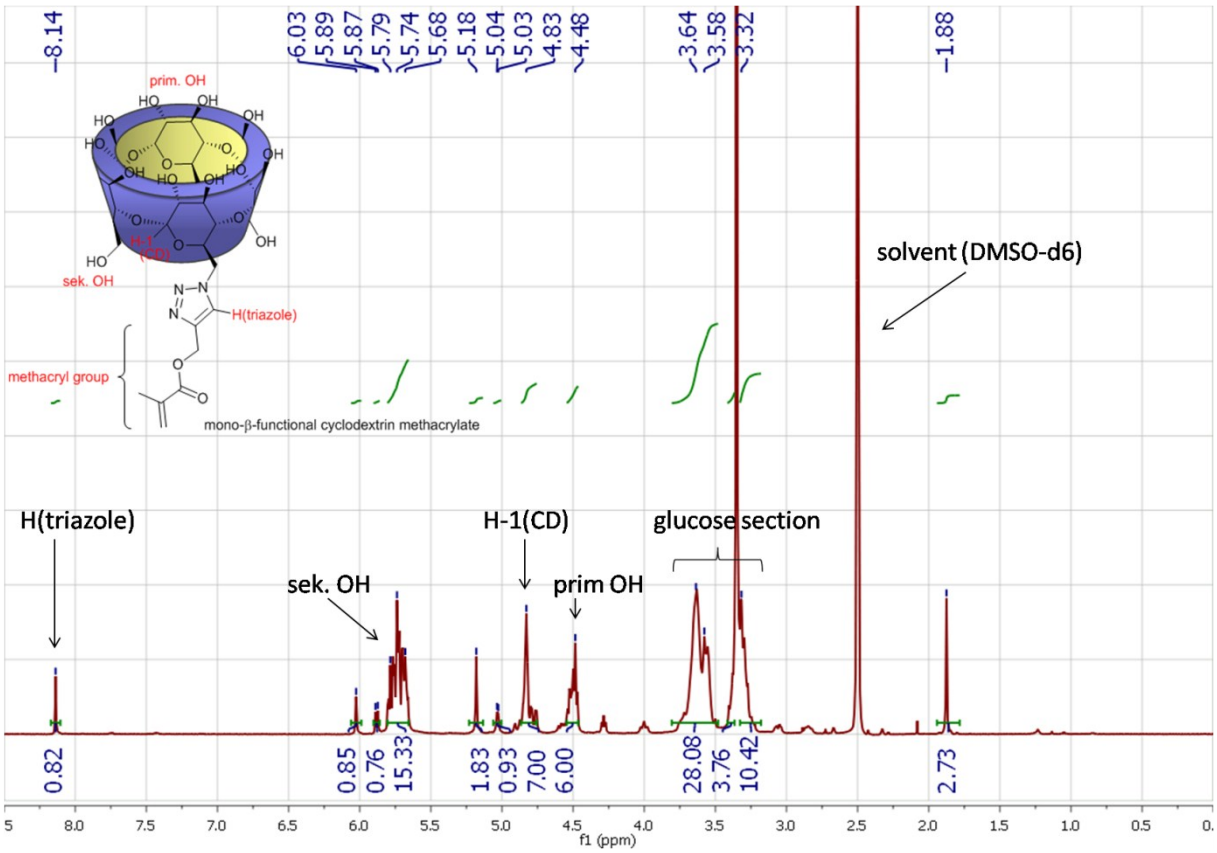


Fig. S2: ^{1}H-NMR spectrum of mβCD-MA in DMSO-d6.

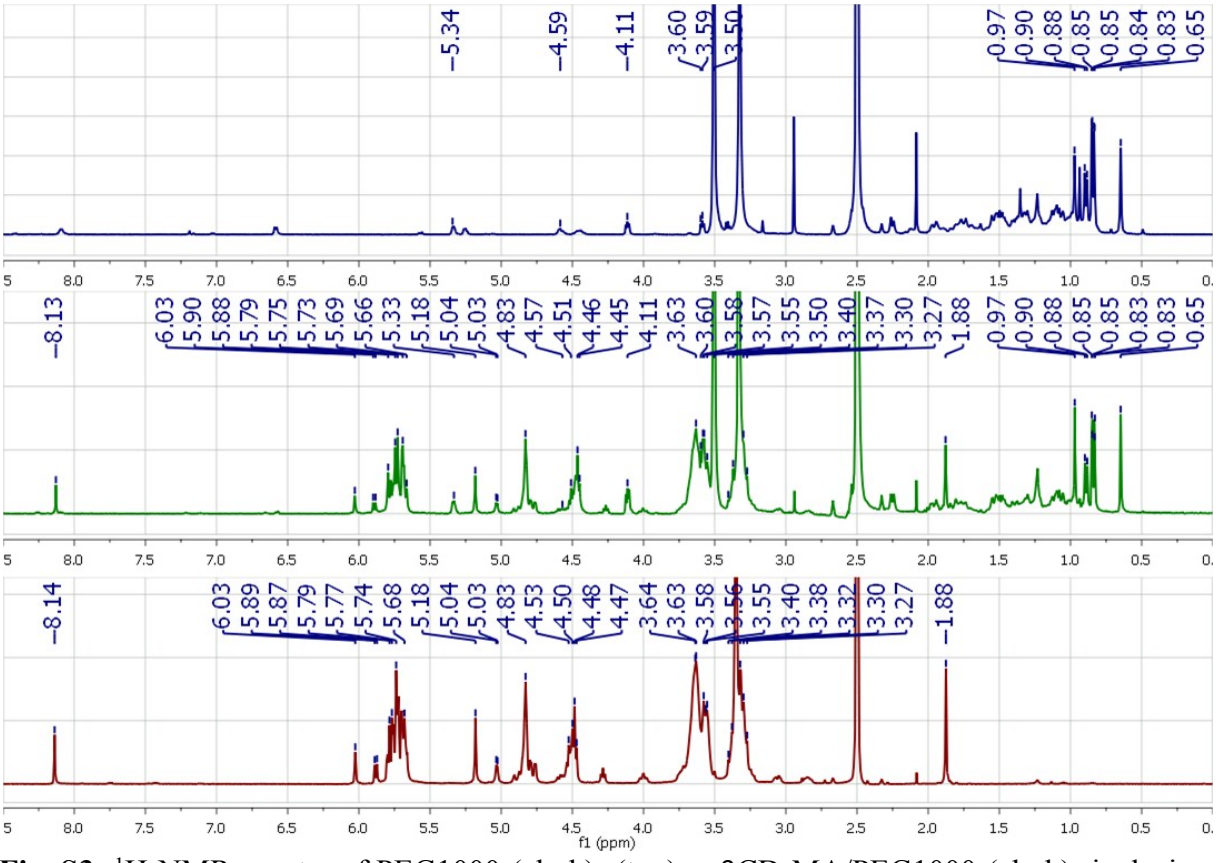


Fig. S3: ^{1}H-NMR spectra of PEG1000-(chol.)$_2$ (top), mβCD-MA/PEG1000-(chol.)$_2$ inclusion complex (middle) and mβCD-MA (bottom) in DMSO-d6.

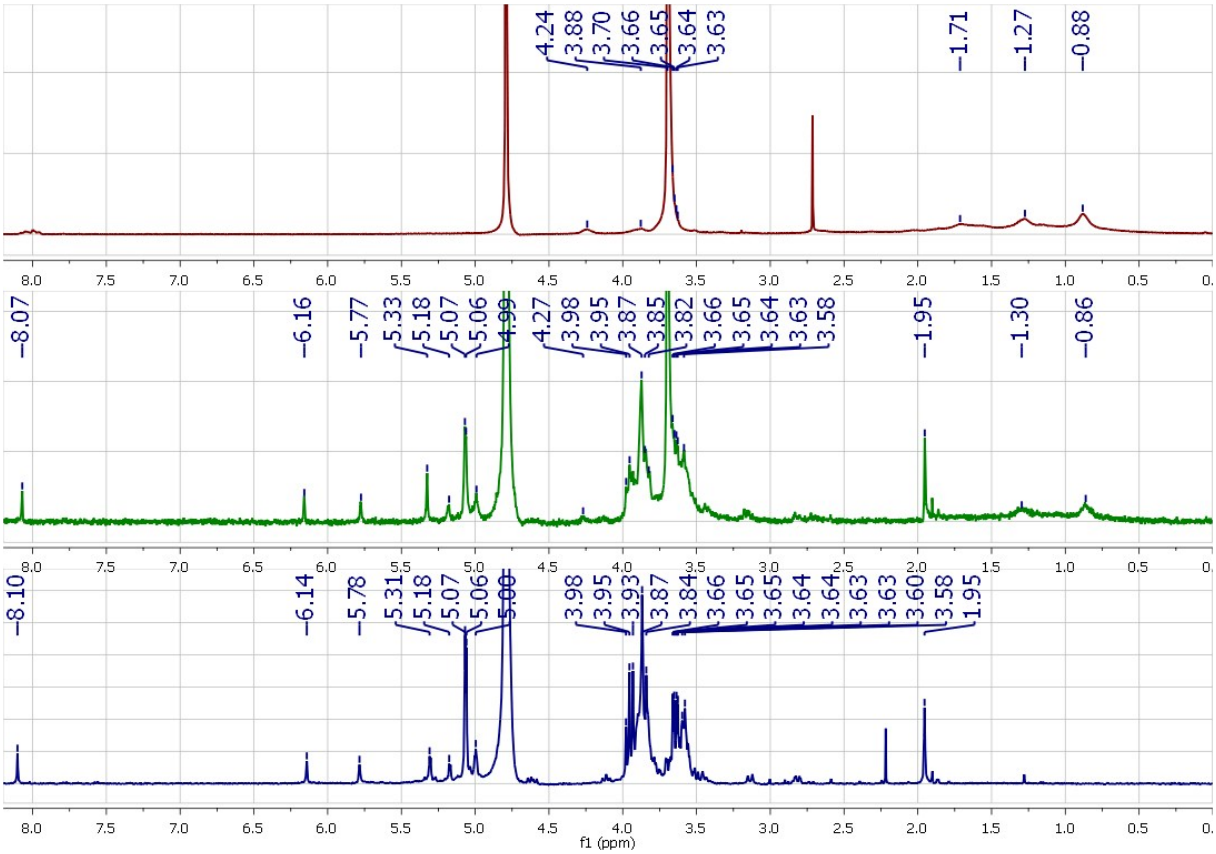
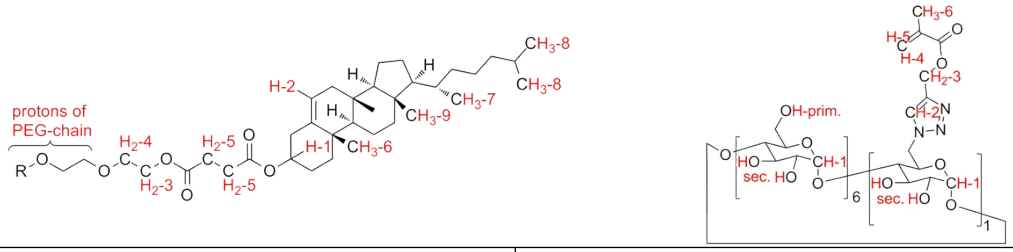


Fig. S4: ^{1}H-NMR spectra of PEG1000-(chol.)$_2$ (top), mβCD-MA/PEG1000-(chol.)$_2$ inclusion complex (middle) and mβCD-MA (bottom) in D_2O.

Tab. S1: Chemical shifts of PEG1000-(chol.)$_2$ and of its inclusion complex in mono-βCD-MA in D_2O.

Protons in PEG1000-(chol.)$_2$	**δ [ppm]**	**Complex in mono-βCD-MA**	
		δ [ppm]	**Δδ [ppm]**
-CH_2- (PEG, H-3)	4.24	4.27	0.03
-CH_2- (cholesteryl)	1.71	-	-
-CH_2- (cholesteryl)	1.27	1.30	0.03
-CH_3 (cholesteryl)	0.88	0.86	-0.02



Protons in m-βCD-MA	**δ [ppm]**	**as guest molecule for PEG1000-(chol.)$_2$**	
		δ [ppm]	**Δδ [ppm]**
H1	5.07	5.07	-
H2	8.10	8.07	-0.03
H3	5.31	5.33	0.02
H4	6.14	6.16	0.02
H5	5.78	5.77	-0.01
H6	1.95	1.95	-

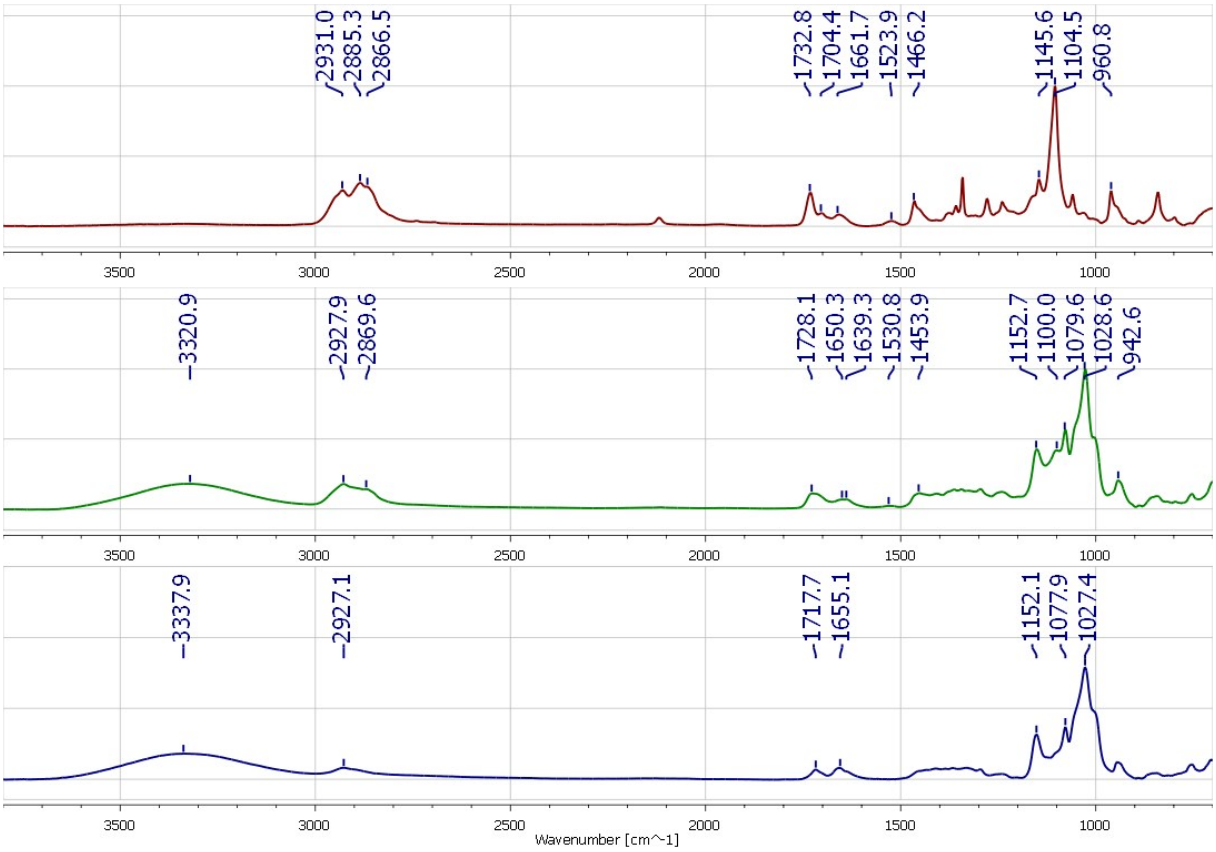


Fig. S5: FT-IR spectra of PEG1000-(chol.)$_2$ (top), mβCD-MA/PEG1000-(chol.)$_2$ inclusion complex (middle) and mβCD-MA (bottom).

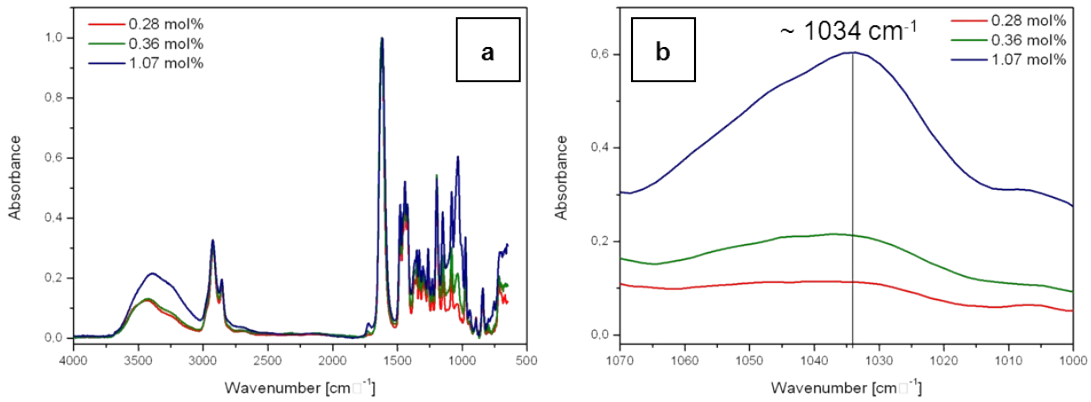


Fig. S6: FT-IR spectra of the different nanogel samples (a) and an excerpt showing the C-O-C-absorption band of β-cyclodextrin (b).

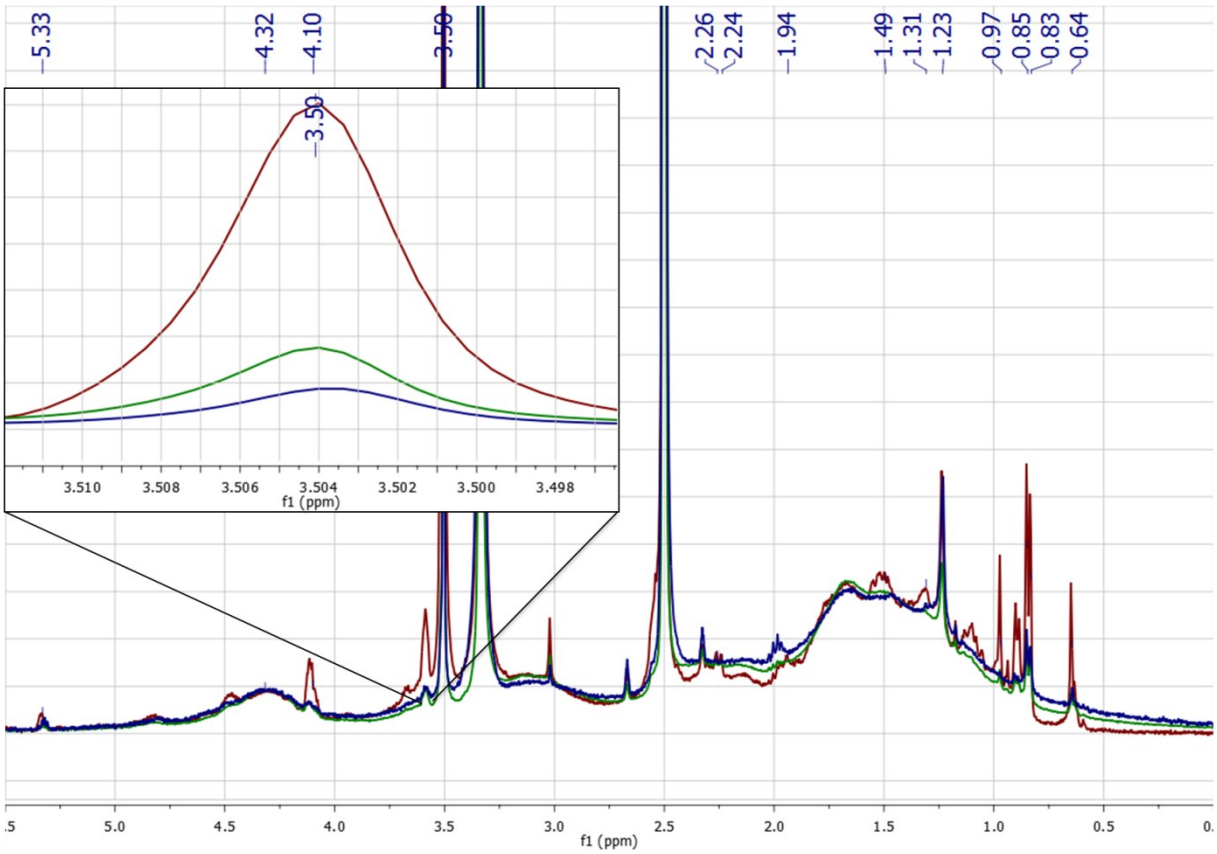


Fig. S7: ^{1}H-NMR spectra of the synthesized microgels, the excerpt shows the -CH_2- signal of the PEG chain.

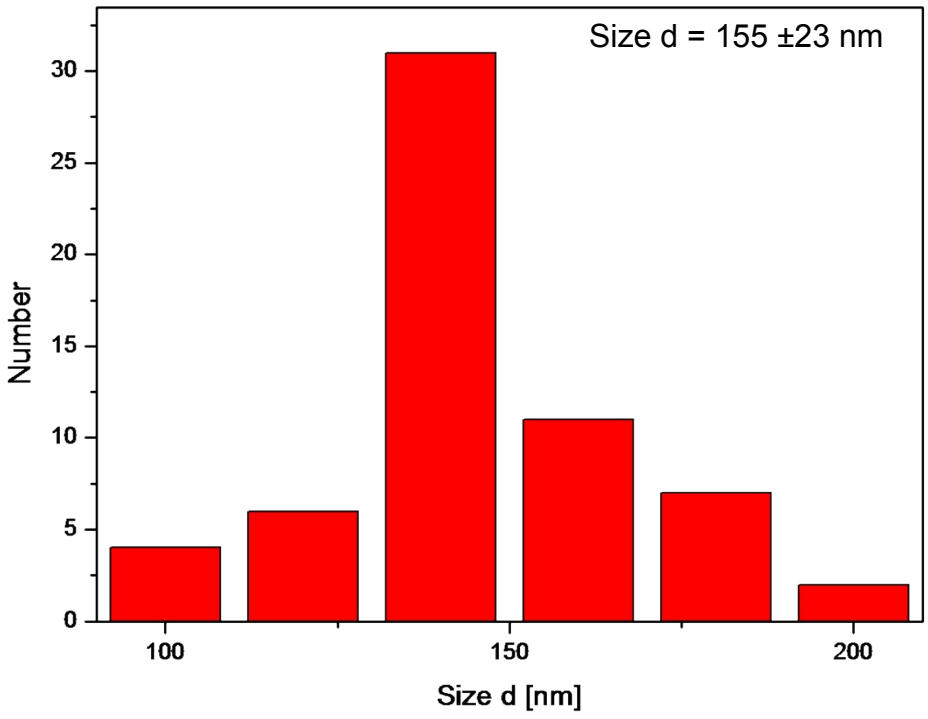


Fig. S8: Particle size distribution determined by electron microscopy (SEM).

Tab. S2: Sample composition of *N,N'*-methylenbisacrylamide (BIS) crosslinked PVCL-microgel, size and solid content.

Sample name	m (*N*-VCL) [g] (mmol)	m (BIS) [g] (mmol)	m (AMPA) [g] (mmol)	Size d [nm] (PDI)	Solid content [mg/mL]
PVCL-BIS-0.85 mol%	0.309 (2.22)	0.003 (0.0193)	0.004 (0.015)	291.9 (0.120)	9.1

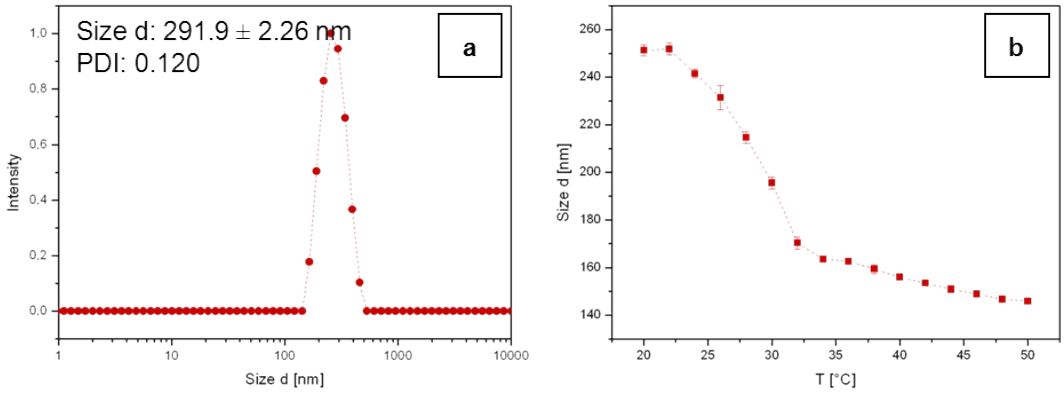


Fig. S9: Size distribution function (a) and temperature dependent size measurement (b) of *N,N'*-methylenbisacrylamide (BIS) crosslinked reference sample.

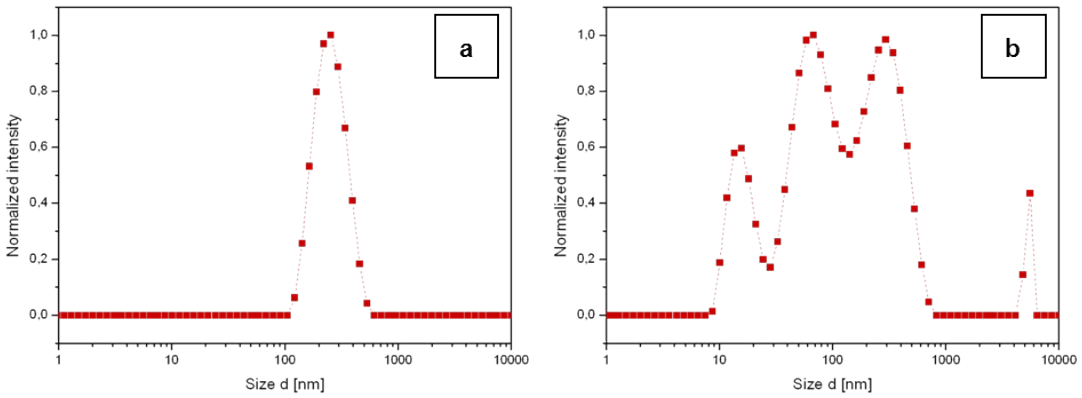


Fig. S10: Size distribution function of PVCL-[mβCD-MA/PEG1000(chol.)$_2$]-1.07 mol% before (a) and after addition of 0.01 mmol AdCOOH/mg microgel (b).

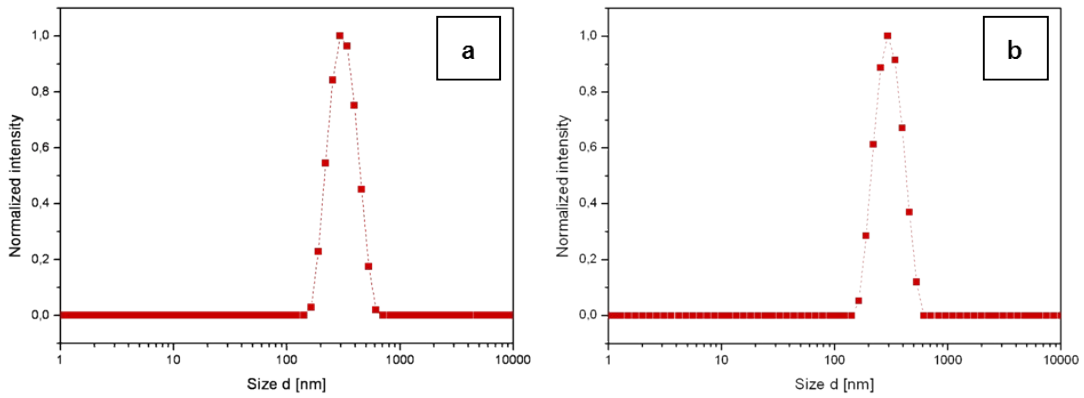


Fig. S11: Size distribution function of PVCL-BIS-0.85 mol% before (a) and after addition of 0.01 mmol AdCOOH/mg microgel (b).

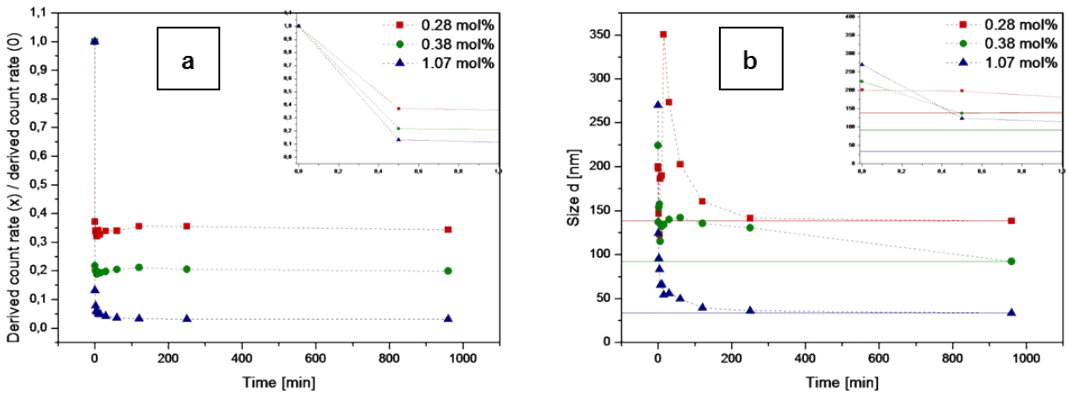


Fig. S12: Time dependent degradation experiments of nanogels with different crosslinker amount (0.01 mmol AdCOOH/ 1.0 mg polymer); monitoring of the derived count rate (a) and the size (b).

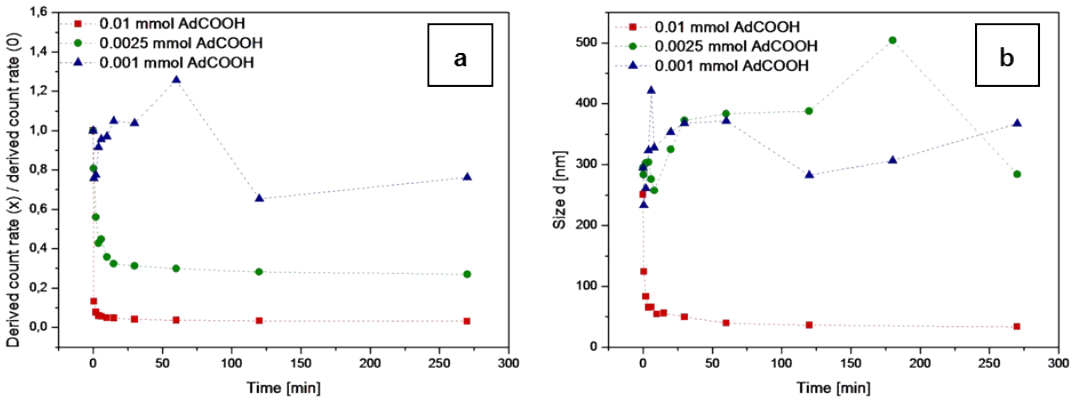


Fig. S13: Time dependent degradation experiments of a nanogel sample containing 1.07 mol% crosslinker at different AdCOOH concentrations; monitoring of the derived count rate (a) and the size (b).

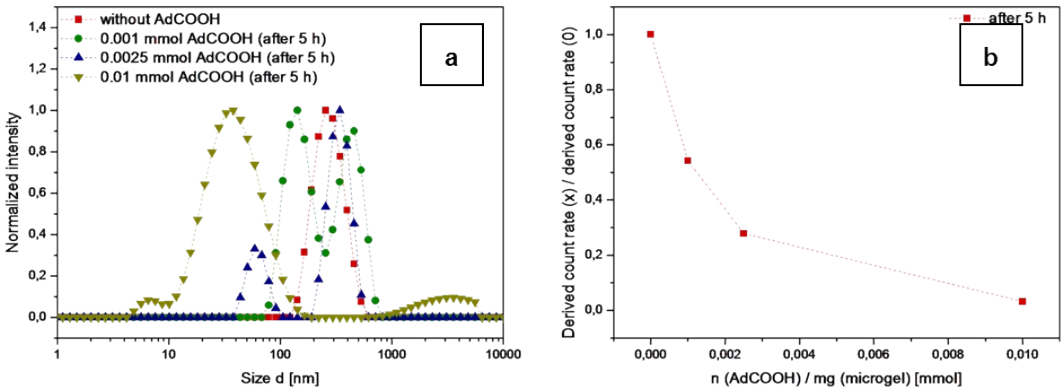


Fig. S14: Size distribution of the different samples after 5 h (a) and relative change of the derived count rate after 5 h using different amounts of AdCOOH (b).

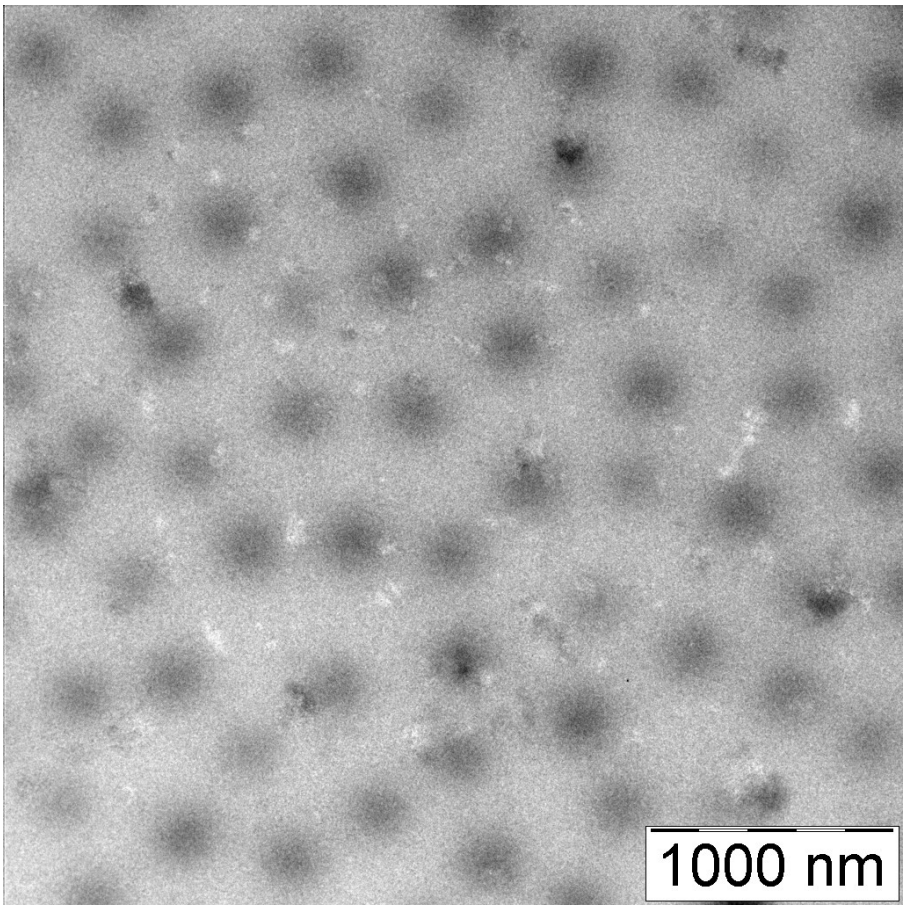


Fig. S15: TEM image of PVCL-[mβCD-MA/PEG1000-(chol.)$_2$]-1.07 mol%, the determined size distribution is 161.053 ±22.145 nm, which is in good agreement with the size determined from the SEM images and the DLS data.