

Supporting Information

Access to Multiblock Copolymers via Supramolecular Host-Guest Chemistry and Photochemical Ligation

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Methods

Materials

Ascorbic acid (99%, Acros), 11-bromoundecanol (97%, ABCR), 3-bromopropionic acid (97%, ABCR), Cs_2CO_3 ($\geq 99.9\%$, Roth), carbon disulfide (CS_2 , $>99.9\%$, VWR), CuBr (99.9%, Acros), *N,N'*-dicyclohexylcarbodiimide (DCC, 99%, Acros), 4-dimethylaminopyridine (DMAP, 99%, Acros), ethanolamine (98%, Acros), K_3PO_4 (Roth), HCl (37%, Roth), 4,10-dioxatricyclo[5.2.1.0]-dec-8-ene-3,5-dione (98%, ABCR), NaHCO_3 ($\geq 99\%$, Roth), MgSO_4 ($\geq 99\%$, Roth), *N,N,N',N',N''*-pentamethyldiethylenetriamine (PMDETA, 99.9%, Merck), 4-*tert.*-butylbenzyl mercaptan (97%, Aldrich) and Quantofix 100 peroxide dipsticks ($1 - 100 \text{ mg L}^{-1} \text{ H}_2\text{O}_2$, Roth) were used as received. Diethylacrylamide (DEAAm, 98%, TCI), dimethylacrylamide (DMAAm, 99%, TCI) and *N*-hydroxyethyl acrylamide (HOEAAM, 97%, Aldrich) were filtered over basic aluminum oxide prior to use and stored at -19°C . Azobisisobutyronitrile (AIBN, 99%, Fluka) was recrystallized twice in methanol and stored at -19°C . *N*-Isopropylacrylamide (NiPAAm, 98%, TCI) was recrystallized in hexane prior to use and stored at -19°C . Milli-Q water was obtained from a purification system by VWR (TKA Micro-Pure; $0.055 \mu\text{S cm}^{-1}$), dichloromethane extra dry (DCM, 99.8% Acros), *N,N*-dimethylformamide extra dry (DMF, 99.8%, Acros), 1,4-dioxane (Sigma Aldrich), methanol extra dry (99.8% Acros) were used as received, as well as DCM, acetone, ethyl acetate (EA), diethyl ether (Et_2O), acetonitrile (MeCN) and cyclohexane (CH) were purchased as analytical grade (VWR). 2-Hydroxy-6-methyl benzaldehyde,¹ 2-(2-hydroxyethyl)-3a,4,7,7a-tetrahydro-1H-4,7-epoxyisoindole-1,3(2H)-dione,^{2,3} 2-(((ethylthio)carbonothioyl)thio)-2-methylpropanoic acid⁴ and prop-2-yn-1-yl 2-(((ethylthio)carbonothioyl)thio)-2-methylpropanoate⁵ were synthesized according to literature procedures.

Characterization

Nuclear Magnetic Resonance (NMR) Spectroscopy

The synthesized structures were confirmed via NMR measurements on a Bruker Ascend 400 spectrometer with 400 MHz for hydrogen nuclei and 100 MHz for carbon nuclei. Samples were dissolved in CDCl_3 , $\text{DMSO-}d_6$ or D_2O . The δ -scale was referenced with tetramethylsilane ($\delta = 0.00$) as internal standard. Abbreviations used below in the description of the materials syntheses include singlet (s), broad singlet (bs), doublet (d), triplet (t), quartet (q), broad multiplet (bm), and unresolved multiplet (m). The 2D NOESY (nuclear Overhauser enhancement spectroscopy) spectrum was measured on a 600 MHz Bruker Avance III

spectrometer equipped with a ^1H , ^{13}C , ^{15}N – TCI inversely detecting cryoprobe at 25 °C (298 K). The 90° proton pulse length was determined to be 8.37 μs . 24 number of scans with 4096 complex data points were recorded for each of the 256 increments with 16 dummy scans per experiment, leading to an overall experiment time of 16 h 49 min 8 sec. Residual protonated water was suppressed using a cw-presaturation sequence with a length of 4 s and an RF amplitude of 25 Hz. Zero filling and linear prediction to a total of 1024 x 1024 complex data points was performed. Processing was achieved using Topspin 3.2. The mixing time was set to 300 μs and the concentration of the sample was 50 mg mL^{-1} in D_2O .

Size Exclusion Chromatography (SEC)

SEC measurements were performed with *N,N*-dimethylacetamide (DMAC) as eluent containing 0.03 wt% LiBr on a Polymer Laboratories PL-GPC 50 Plus Integrated System, comprising an autosampler, a PLgel 5 μm bead-size guard column (50 \times 7.5 mm) followed by three PLgel 5 μm MixedC columns (300 \times 7.5 mm), and a differential refractive index detector at 50 °C with a flow rate of 1.0 mL min^{-1} . The SEC system was calibrated against linear poly(styrene) standards with molecular weights ranging from 160 to 6 \cdot 10⁶ g mol^{-1} . Calculations for the molecular weight of poly(DMAAm)-*t*BuBnPE and poly(DEAAm)-Mal were carried out according to a poly(styrene) calibration, i.e. $K = 14.1 \cdot 10^{-5} \text{ dL g}^{-1}$, $\alpha = 0.70$ (PS).⁶⁰ The molecular weight dispersity is abbreviated as \mathcal{D} .

Electrospray Ionization-Mass Spectrometry (ESI-MS)

Mass spectra were recorded on a Q Exactive (Orbitrap) mass spectrometer (Thermo Fisher Scientific, San Jose, CA, USA) equipped with an HESI II probe. The instrument was calibrated in the m/z range 74-1822 using premixed calibration solutions (Thermo Scientific). A constant spray voltage of 4.7 kV and a dimensionless sheath gas of 5 were applied. The capillary temperature and the S-lens RF level were set to 320 °C and 62.0, respectively. The samples were dissolved with a concentration of 0.05 mg mL^{-1} in a mixture of THF and MeOH (3:2) containing 100 μmol of sodium trifluoroacetate (NaTFA) and infused with a flow of 5 $\mu\text{L min}^{-1}$.

Dynamic Light Scattering (DLS)

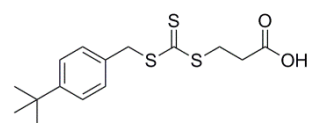
Sample solutions were prepared by dissolving the samples in Milli Q water at a constant concentration of 0.06 mmol L^{-1} . The solutions were filtered via a 0.2 μm syringe filter to remove dust particles. Before the measurement the solution of the supramolecular triblock copolymer was left for 30 min, so the equilibrium between β -CD and *tert*-butyl phenyl units

could re-establish. Hydrodynamic diameters were determined via dynamic light scattering (Nicomp 380 DLS spectrometer from Particle Sizing Systems, Santa Barbara, USA, laser diode: 90 mW, 658 nm). Measurements were performed in automatic mode and evaluated with a standard Gaussian and an advanced evaluation method, the latter proceeding via an inverse Laplace algorithm to analyze for multimodal distributions. The values provided in the study are the number-weighted average values as calculated in the NICOMP evaluation. All measurements were determined at an angle of 90° to the incident beam. The associated auto-correlation functions can be found in Figure S29 to Figure S42.

UV-vis Spectrometer

UV-Vis spectra were measured on a Cary 300 Bio UV-Vis spectrophotometer (Varian) at either 25 °C or 10 °C, depending on the sample.

Experimental Section



3-((((4-tert-butylbenzyl)thio)carbonothioyl)thio)propanoic acid

(I): 4-*tert*-butylbenzyl mercaptan (5.50 g, 30.50 mmol, 1.10 eq.) was added to a suspension of K₃PO₄ (8.25 g, 38.80 mmol, 1.40 eq.) in

acetone (150 mL) and stirred for 20 min at ambient temperature. Subsequently, CS₂ (6.54 g, 86.00 mmol, 3.10 eq.) was added to the reaction mixture, which turned yellow. After another 20 min of stirring, 3-bromopropanoic acid (4.25 g, 27.70 mmol, 1.00 eq.), dissolved in acetone (10 mL), was added to the suspension and the reaction was stirred at 40 °C overnight. HCl (1 M, 100 mL) was added to the reaction mixture and the aqueous solution was extracted with DCM (2 × 150 mL). The combined organic extracts were washed with deionized water (150 mL) and brine (150 mL) and dried over MgSO₄. After evaporation of the solvent the yellow oil was purified via column chromatography on silica gel in a mixture of cyclohexane and ethyl acetate which was gradually changed from 3:1 to 1:1 to result in a yellow oil which solidified in the freezer (8.62 g, 94%). ¹H NMR (400 MHz, DMSO-*d*₆): δ = 12.51 (bs, 1 H, COOH); 7.36 – 7.29 (m, 4 H, Ar-H); 4.64 (s, 2 H, Ar-CH₂-S); 3.54 (t, 2 H, ³J_{HH} = 6.9 Hz, S-CH₂-CH₂); 2.68 (t, 2 H, ³J_{HH} = 6.9 Hz, CH₂-CO); 1.26 (s, 9 H, C-C₃H₉) ppm. ¹³C NMR (400 MHz, DMSO-*d*₆): δ = 223.92 (C=S), 172.91 (O-C-OH), 130.68 (C_{Ar}-C₄H₉), 132.41 (C_{Ar}-CH₂), 129.28 (C_{Ar}), 125.90 (C_{Ar}), 34.72 (C_{Ar}-CH₂-S), 32.83 (CH₂, C-C₃H₉), 32.14 (S-CH₂), 31.32 (C-C₃H₉) ppm.

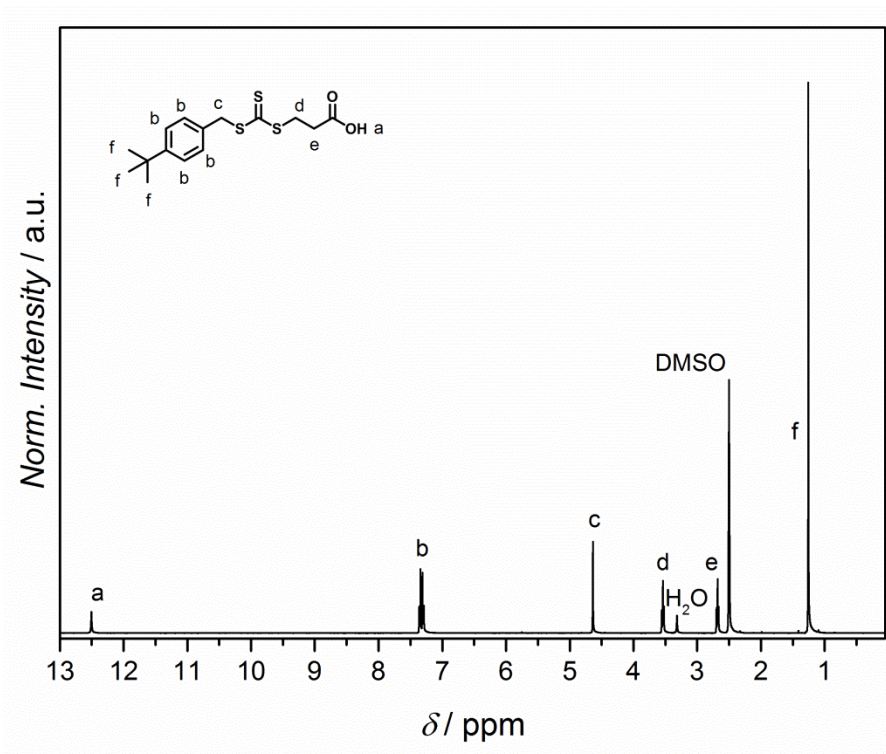


Figure S1. ^1H NMR spectrum (400 MHz, $\text{DMSO-}d_6$, 25 °C) of 3-(((4-(tert-butyl)benzyl)thio)carbonothioyl)thio)propanoic acid (**1**).

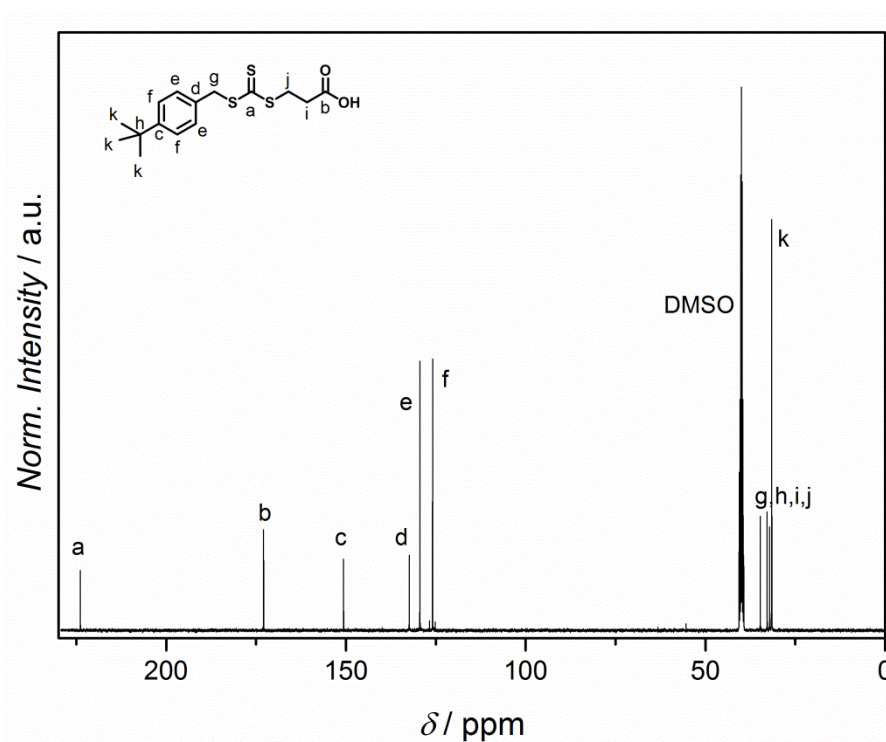
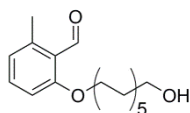


Figure S2. ^{13}C NMR spectrum (400 MHz, $\text{DMSO-}d_6$, 25 °C) of 3-(((4-(tert-butyl)benzyl)thio)carbonothioyl)thio)propanoic acid (**1**).



2-((11-Hydroxyundecyl)oxy)-6-methylbenzaldehyde (**2**): Cs₂CO₃ (3.25 g, 9.97 mmol, 1.67 eq.) was suspended in dry DMF (20 mL). 2-Hydroxy-6-methyl benzaldehyde (1.02 g, 7.46 mmol, 1.25 eq.) was added and the mixture was stirred for 20 min at ambient temperature. Subsequently, a solution of 1-bromoundecanol (1.50 g, 5.97 mmol, 1.00 eq.) in dry DMF (5 mL) was added dropwise to the suspension and the reaction proceeded at 50 °C overnight. The solvent was evaporated under reduced pressure. Next, the residue was dissolved in diethyl ether and washed three times with brine (50 mL). The organic phase was dried over MgSO₄ and the solvent was evaporated. The crude product was purified via column chromatography with a mixture of cyclohexane/ethyl acetate (2:1). The product was obtained as a slightly yellow solid (1.66 g, 90% yield). ¹H NMR (400 MHz, CDCl₃): δ = 10.63 (s, 1 H, CHO), 7.35 (t, 1 H, ³J_{HH} = 7.9 Hz, Ar-H), 6.82-6.77 (m, 2 H, Ar-H), 4.04 (t, 2 H, ³J_{HH} = 6.3 Hz, O-CH₂), 3.64 (t, 2 H, ³J_{HH} = 6.6 Hz, CH₂-OH), 2.57 (s, 3 H, Ar-CH₃), 1.82 (quin., 2 H, ³J_{HH} = 6.5 Hz, OCH₂-CH₂), 1.58-1.57 (m, 2 H, CH₂), 1.49-1.43 (m, 2 H, C₅H₁₀-CH₂), 1.38-1.28 (m, 12 H, CH₂) ppm. ¹³C NMR (400 MHz, CHCl₃): δ = 192.57 (CHO), 162.90 (HC_{Ar}-C_{Ar}-O), 141.98 (C_{Ar}-CH₃), 134.43 (C_{Ar}-CH-C_{Ar}), 123.85 (C_{Ar}-CHO), 123.39 (C_{Ar}-C_{Ar}-CH₃), 109.90 (C_{Ar}-C_{Ar}-O), 68.67 (O-CH₂-CH₂), 63.09 (CH₂-OH), 32.81 (CH₂-CH₂-OH), 29.49 (CH₂-C₅H₁₀-CH₂), 29.15 (O-CH₂-CH₂), 26.10 (O-C₂H₄-CH₂), 25.72 (CH₂-C₂H₄-OH), 21.54 (Ar-CH₃) ppm. MS: (ESI) *m/z* calculated for C₁₉H₃₀O₃ [M+Na]⁺: 329.21, found 329.28.¹

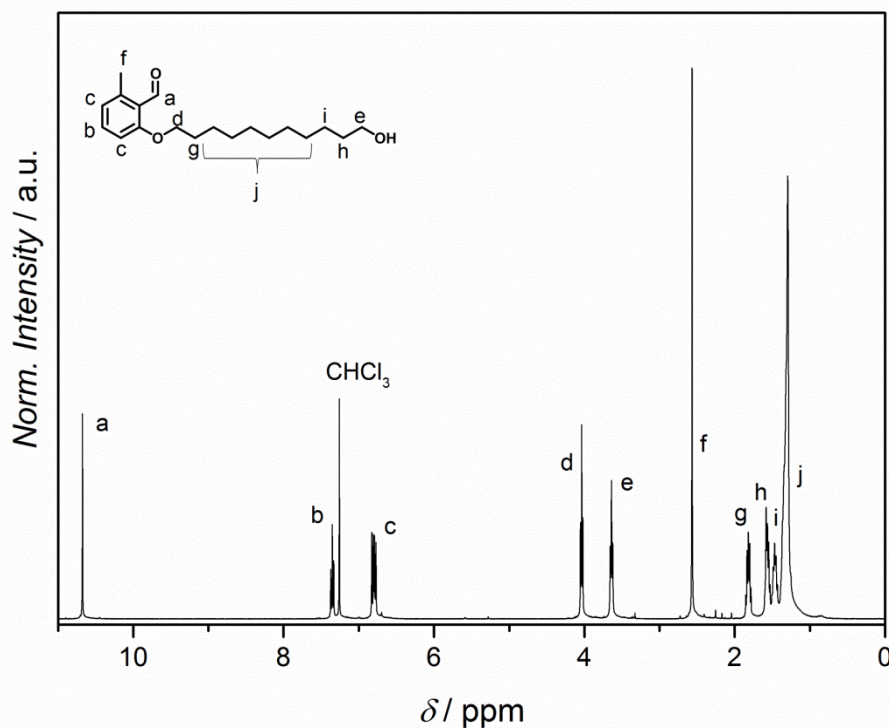


Figure S3. ¹H NMR spectrum (400 MHz, CDCl₃, 25 °C) of 2-((11-hydroxyundecyl)oxy)-6-methylbenzaldehyde (**2**).

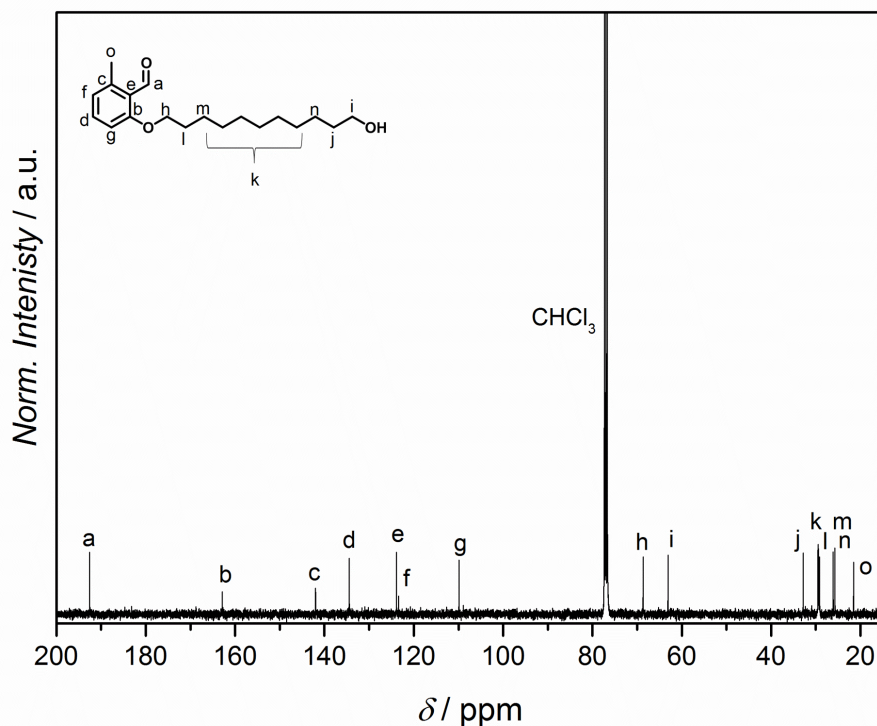


Figure S4. ^{13}C NMR spectrum (400 MHz, CDCl_3 , 25 °C) of 2-((11-hydroxyundecyl)oxy)-6-methylbenzaldehyde (**2**).

*Synthesis of 11-(2-formyl-3-methylphenoxy)undecyl 3-(((4-(tert-butyl)benzyl)thio)carbonothioyl)thio)propanoate (tBuBnPE-trithiocarbonate) (**3**):* 3-(((4-(tert-butyl)benzyl)thio)carbonothioyl)thio)propanoic acid (**1**) (787.89 mg, 2.39 mmol, 1.5 eq.) 2-((11-hydroxyundecyl)oxy)-6-methylbenzaldehyde (**2**) (490.00 mg, 1.59 mmol, 1.0 eq.) and DMAP (3.91 mg, 0.03 mmol, 0.02 eq.) were dissolved in dry DCM (10 mL). Subsequently, a solution of DCC (494.87 mg, 2.39 mmol, 1.5 eq.) in dry DCM (5 mL) was added dropwise to the reaction mixture at 0 °C. The reaction was covered with aluminum foil and the mixture was stirred overnight at ambient temperature. The suspension was filtered, washed with aqueous HCl (5%), NaHCO_3 solution and deionized water. The organic phase was dried over MgSO_4 and the solvent was removed under reduced pressure. The crude product was purified via column chromatography in cyclohexane/ethyl acetate (5:1) to give a yellow oil (868.10 mg, 88%). ^1H NMR (400 MHz, CHCl_3): δ = 10.68 (s, 1 H, CHO), 7.29-7.29 (m, 3 H, Ar-H), 7.17 (d, 2 H, $^3J_{\text{HH}} = 8.2$ Hz, Ar-H), 6.74-6.69 (m, 2 H, Ar-H), 4.74 (q, 1 H, $^3J_{\text{HH}} = 7.4$ Hz, S-CH-CH₃), 4.49 (s, 2 H, Ar-CH₂-S), 4.09-4.03 (m, 2 H, O-CH₂-CH₂), 3.95 (t, 2 H, $^3J_{\text{HH}} = 6.4$ Hz, CH₂-CH₂-O), 2.49 (s, 3 H, Ar-CH₃), 1.77-1.71 (m, 2 H, H₁₄C₇-CH₂-CH₂O), 1.58-1.52 (m, 3 H, CH₃-C-S), 1.49-1.45 (m, 2 H, O-CH₂-CH₂-C₇H₁₁), 1.30-1.26 (m, 23 H, C₇H₁₁,

C_3H_9) ppm. ^{13}C NMR (400 MHz, $CHCl_3$) δ = 223.23 (C=S), 192.53 (H-C=O), 171.50 (O-C=O), 162.89 (O-C_{Ar}), 150.88 (C_{Ar}-C₄H₉), 141.96 (C_{Ar}-CH₃), 134.43 (C_{Ar}), 131.68 (C_{Ar}-CH₂), 128.97 (C_{Ar}), 125.69 (C_{Ar}-CHO), 123.85 (C_{Ar}), 123.40 (C_{Ar}), 109.91 (C_{Ar}), 68.67 (CH₂-CH₂-O), 65.15 (O-CH₂-CH₂), 41.26 (C_{Ar}-CH₂-S), 34.57 (CH₂-CH₂-CO), 33.21 (C-C₃H₉), 31.40 (C₃H₉), 29.47 (CH₂-CH₂-CH₂), 29.33 (CH₂-C₅H₁₀-CH₂), 28.55 (CH₂-CH₂-CH₂), 26.11 (CH₂-CH₂-CH₂), 25.89 (S-CH₂-CH₂), 21.55 (CH₃-C_{Ar}) ppm. MS (ESI) m/z calculated for $C_{32}H_{48}O_4S_3$ [M+Na]⁺: 639.26, found 639.28.

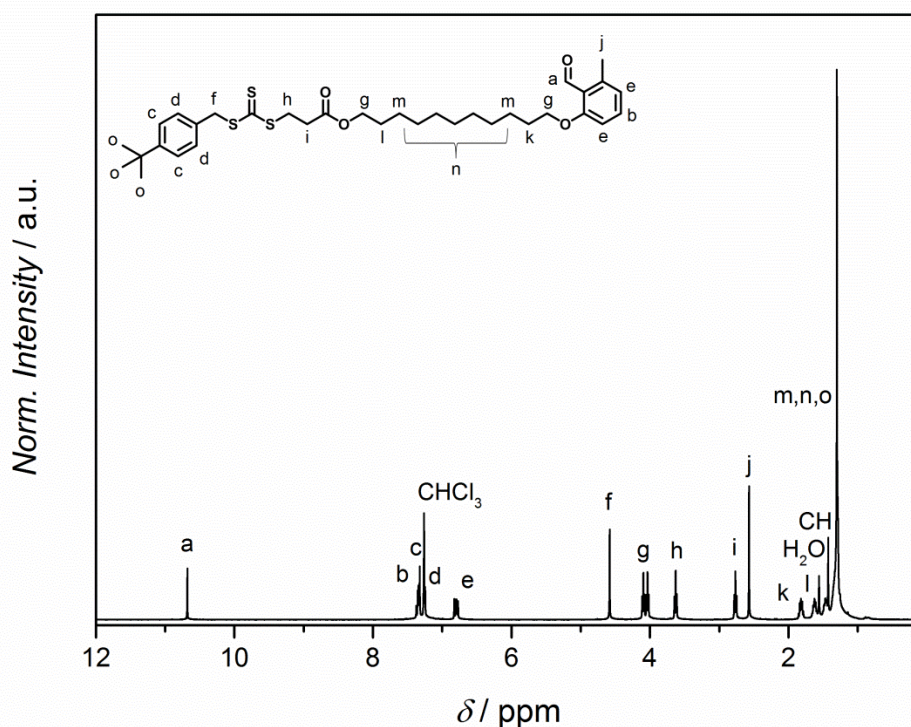


Figure S5. 1H NMR spectrum (400 MHz, $CDCl_3$, 25 °C) of 11-(2-formyl-3-methylphenoxy)undecyl 3-(((4-(*tert*-butyl)benzyl)thio)carbonothioyl)thio)propanoate (*t*BuBnPE-trithiocarbonate) **3**.

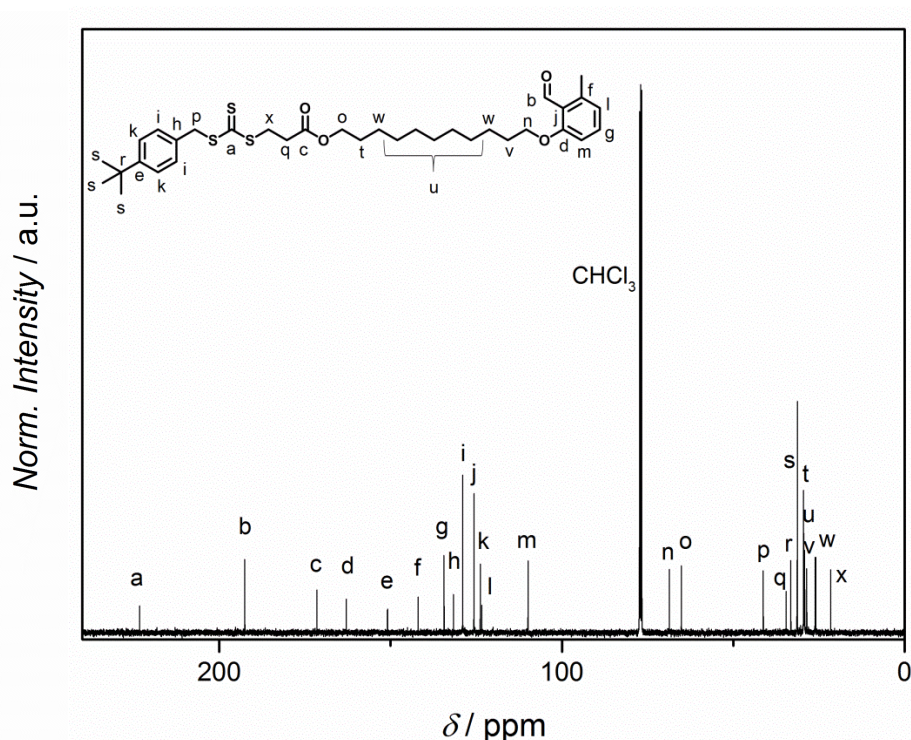
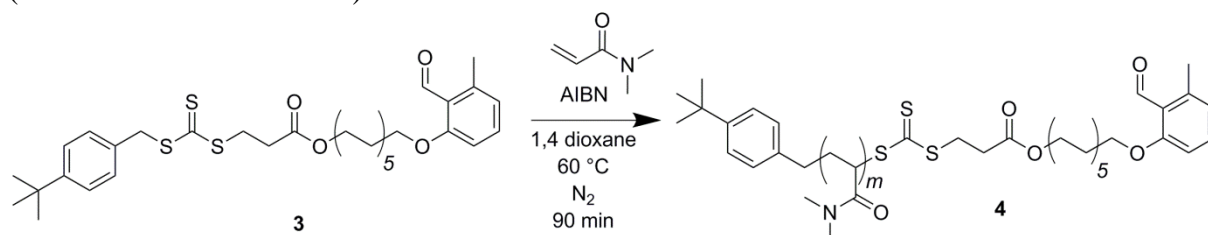


Figure S6. ^{13}C NMR spectrum (400 MHz, CDCl_3 , 25 °C) of 11-(2-formyl-3-methylphenoxy)undecyl 3-(((4-(*tert*-butyl)benzyl)thio)carbonothioyl)thio)propanoate (*t*BuBnPE-trithiocarbonate) **3**.



Scheme S1. Synthesis route for poly(DMAAm)-*t*BuBnPE **4**.

Poly(DMAAm)-tBuBnPE (**4**): *t*BuBnPE-trithiocarbonate **3** (74.04 mg, 0.12 mmol, 1.00 eq.), AIBN (1.90 mg, 11.93 μmol , 0.10 eq.) and DMAAm (1.00 g, 10.09 mmol, 84.62 eq.) were dissolved in 1,4-dioxane (1.10 mL). The yellow solution was added to a Schlenk-tube and oxygen was removed from the mixture via three freeze pump thaw cycles. Subsequently, the sample was placed in a preheated oil bath at 60 °C for 90 min. The reaction was quenched by cooling on ice and subsequently dialyzed against deionized water with a SpectraPor3 membrane (MWCO = 1000 Da) for three days at ambient temperature. After lyophilization of the aqueous solution, the pure product was obtained as yellowish powder (745.00 mg, M_n *theo* = 9000 g mol^{-1} , M_n *SEC* (DMAC) = 7300 g mol^{-1}).

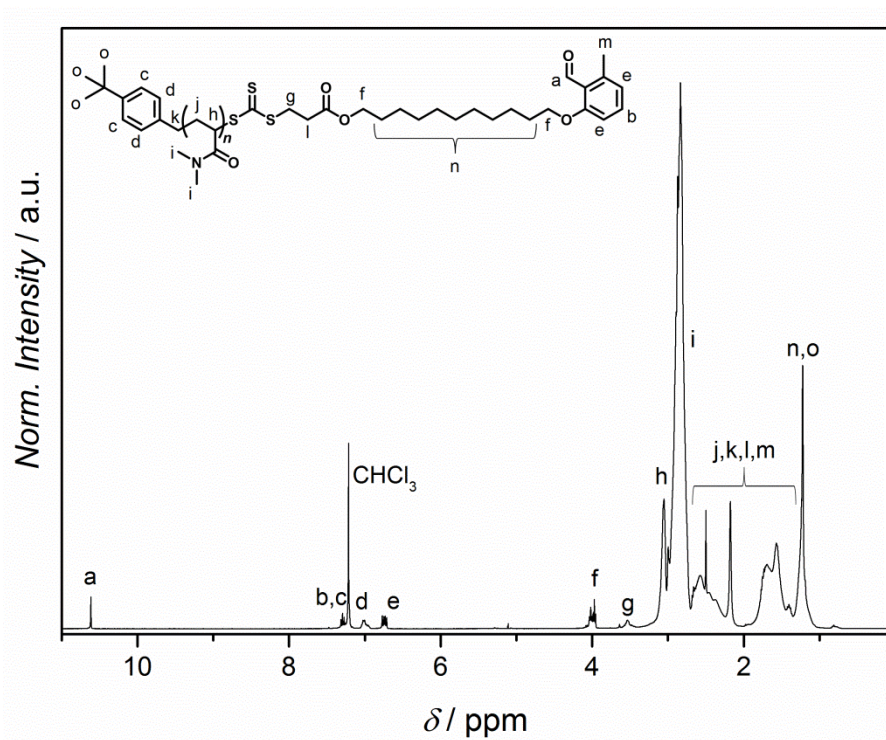


Figure S7. ^1H NMR spectrum (400 MHz, CDCl_3 , 25 $^\circ\text{C}$) of poly(DMAAm)-*t*BuBnPE (**4**).

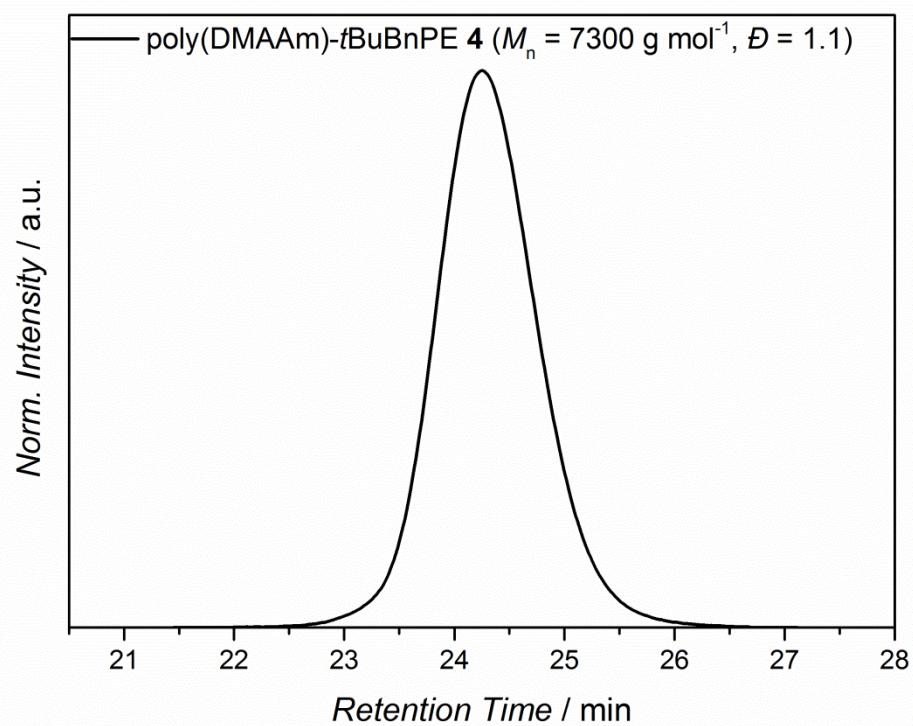


Figure S8. SEC trace of poly(DMAAm)-*t*BuBnPE **4** measured in DMAC at 50 $^\circ\text{C}$.

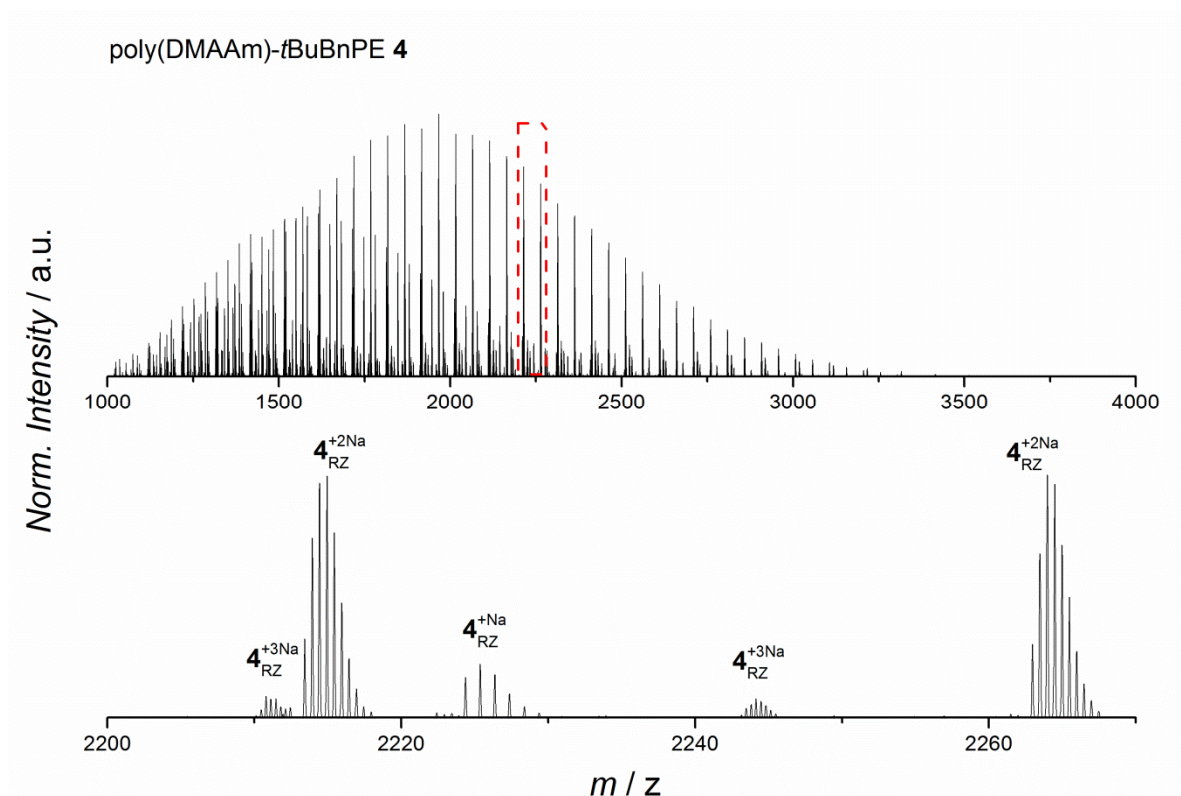
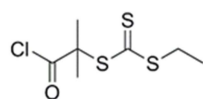


Figure S9. ESI-MS spectrum of poly(DMAAm)-*t*BuBnPE **4** (above) and a magnification of the spectrum (below). The spectrum shows the single, double and triple charged polymer chains of the product **4**, ionized with Na⁺.

Table S1. Mass peak assignment for poly(DMAAm)-*t*BuBnPE **4**. Experimental and theoretical m/z values for the labelled peaks shown in **Figure S9**.

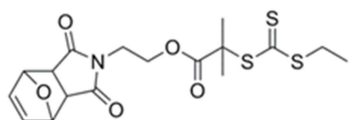
| m/z_{exp} | assignment | chemical formula | m/z_{theo} | $\Delta m/z$ |
|--------------------|---|---|---------------------|--------------|
| 2211.129 | p(DMAAm)- <i>t</i> BuBnPE + Na ₃ | [C ₃₃₄ H ₅₈₈ N ₆₀ Na ₃ O ₆₄ S ₃] ³⁺ | 2211.119 | 0.01 |
| 2214.437 | p(DMAAm)- <i>t</i> BuBnPE + Na ₂ | [C ₂₂₄ H ₃₉₀ N ₃₈ Na ₂ O ₄₂ S ₃] ²⁺ | 2214.428 | 0.009 |
| 2225.365 | p(DMAAm)- <i>t</i> BuBnPE + Na | [C ₁₁₄ H ₁₉₂ N ₁₆ NaO ₂₀ S ₃] ⁺ | 2225.358 | 0.007 |
| 2244.152 | p(DMAAm)- <i>t</i> BuBnPE + Na ₃ | [C ₃₃₉ H ₅₉₇ N ₆₁ Na ₃ O ₆₅ S ₃] ³⁺ | 2244.142 | 0.01 |
| 2263.970 | p(DMAAm)- <i>t</i> BuBnPE + Na ₂ | [C ₂₂₉ H ₃₉₉ N ₃₉ Na ₂ O ₄₃ S ₃] ²⁺ | 2263.962 | 0.008 |



Synthesis of 1-chloro-2-methyl-1-oxopropan-2-yl ethyl carbonotrithioate: 2-(((ethylthio)carbonothioyl)thio)-2-methylpropanoic acid (3.00 g,

13.30 mmol, 1.0 eq) was placed in a round bottom Schlenk-flask, evacuated and flooded with nitrogen. The substance was dissolved in dry DCM (90 mL) with the addition of 0.5 mL DMF. At 0 °C oxalyl chloride (3.50 mL, 18.6 mmol, 1.4 eq.) was slowly added to the

solution. The reaction was allowed to warm to ambient temperature and stirred overnight. The solvent was removed in vacuo and the obtained product (3.25 g, 99%) was used directly for the synthesis of 2-(1,3-dioxo-1,3,3a,4,7,7a-hexahydro-2H-4,7-epoxyisoindol-2-yl)ethyl 2-(((ethylthio)carbonothioyl)thio)-2-methylpropanoate.



Synthesis of 2-(1,3-dioxo-1,3,3a,4,7,7a-hexahydro-2H-4,7-epoxyisoindol-2-yl)ethyl 2-(((ethylthio)carbonothioyl)thio)-2-methylpropanoate (Mal-trithiocarbonate) (5i):

In a round bottom Schlenk-flask under a nitrogen atmosphere 2-(2-hydroxyethyl)-3a,4,7,7a-tetrahydro-1H-4,7-epoxyisoindole-1,3(2H)-dione (2.78 g, 13.3 mmol, 1.1 eq.) was dissolved in dry DCM (30 mL), cooled to 0 °C in an ice bath and triethylamine (3.72 mL, 13.17 mmol, 1.0 eq) was added dropwise to the solution. Subsequently, 1-chloro-2-methyl-1-oxopropan-2-yl ethyl carbonotrithioate (3.25 g, 13.17 mmol, 1.0 eq.), dissolved in dry DCM (40 mL), was added dropwise to the mixture, which was stirred overnight at ambient temperature. DCM (50 mL) was added to the reaction and the mixture was washed with NaHCO₃ solution, deionized water and brine and dried over MgSO₄. The solvent was removed under reduced pressure and the crude product was purified via column chromatography in a mixture of *n*-hexane/ ethyl acetate (1:1). The pure product was obtained as yellow solid (2.33 g, 49%). ¹H NMR (400 MHz, CDCl₃) δ = 6.51 (s, 2 H, **HC=CH**), 5.26 (s, 2 H, **HC-O-CH**), 4.26 (t, 2 H, ³J_{HH} = 5.3 Hz, CH₂-CH₂-O), 3.78 (t, 2 H, ³J_{HH} = 5.4 Hz, N-CH₂-CH₂), 3.26 (q, 2 H, ³J_{HH} = 7.4 Hz, S-CH₂-CH₃), 2.86 (s, 2 H, **HC-CH**), 1.65 (s, 6 H, C₂H₆), 1.31 (t, 3 H, ³J_{HH} = 7.4 Hz, CH₂-CH₃) ppm. ¹³C NMR (400 MHz, CDCl₃) δ = 221.51 (C=S), 175.82 (N-C=O), 172.70 (O-C=O), 136.56 (C=C), 80.87 (C-O-C), 62.17 (CH₂-CH₂-O), 55.95 (HC-CH), 47.54 (C₂H₆-C-S), 37.57 (N-CH₂), 31.25 (S-CH₂-CH₃), 25.13 (C-C₂H₆), 12.88 (CH₂-CH₃) ppm.

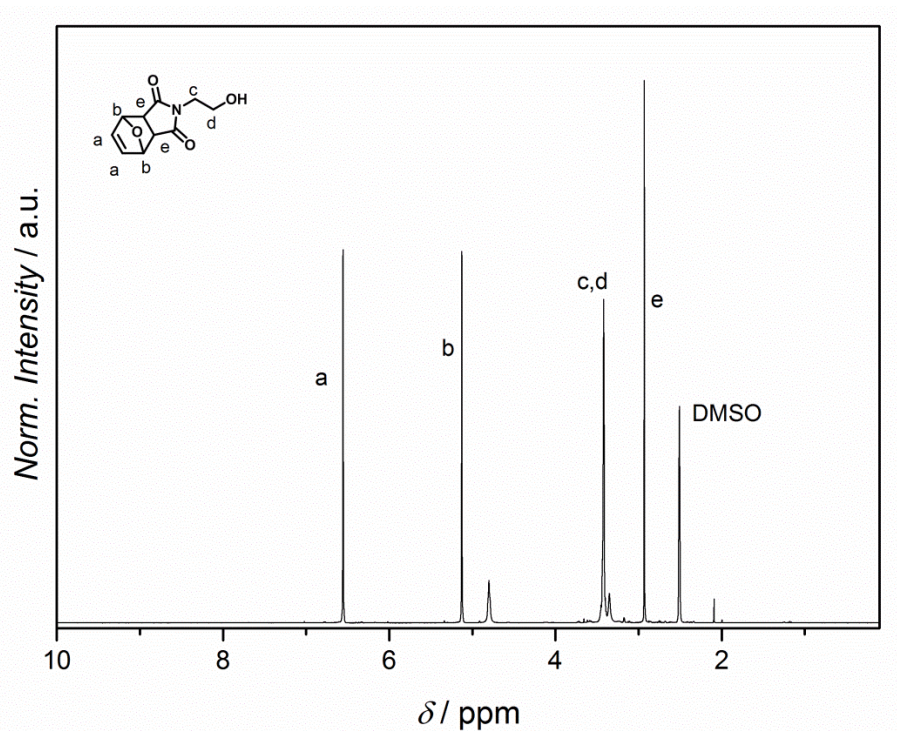


Figure S10. ^1H NMR spectrum (400 MHz, DMSO- d_6 , 25 °C) 2-(2-hydroxyethyl)-3a,4,7,7a-tetrahydro-1H-4,7-epoxyisoindole-1,3(2H)-dione.

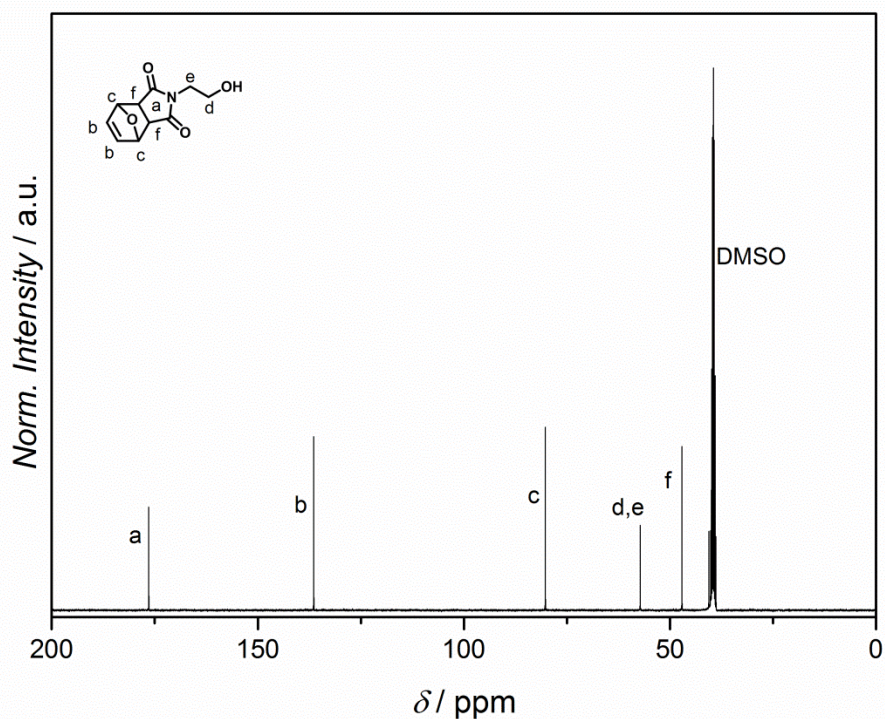


Figure S11. ^{13}C NMR spectrum (400 MHz, DMSO- d_6 , 25 °C) 2-(2-hydroxyethyl)-3a,4,7,7a-tetrahydro-1H-4,7-epoxyisoindole-1,3(2H)-dione

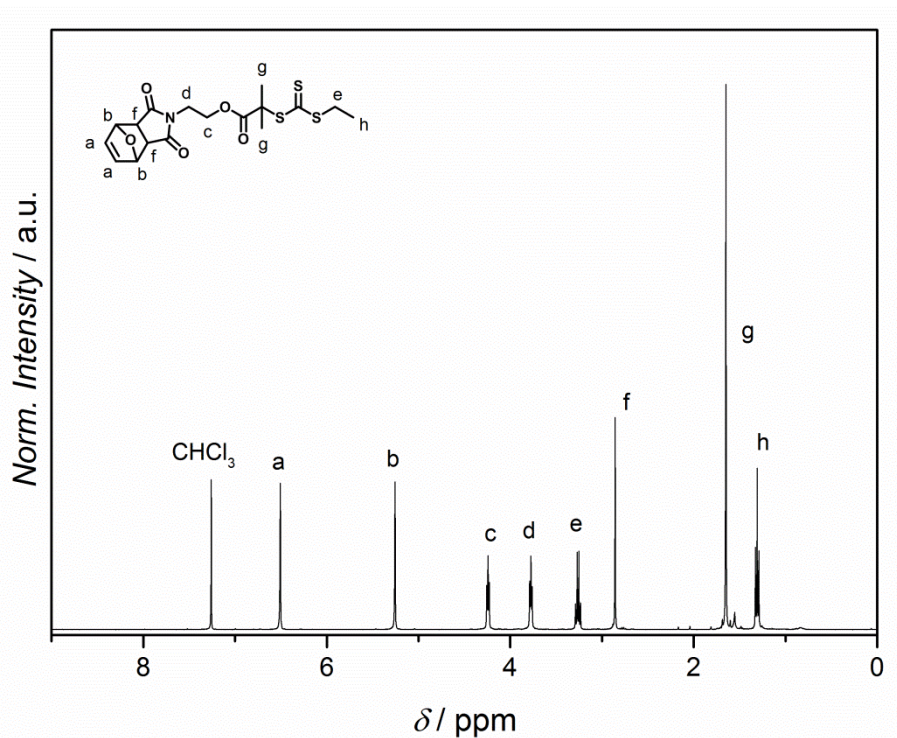


Figure S12. ^1H NMR spectrum (400 MHz, CDCl_3 , 25 °C) of 2-(1,3-dioxo-1,3,3a,4,7,7a-hexahydro-2H-4,7-epoxyisoindol-2-yl)ethyl 2-(((ethylthio)carbonothioyl)thio)-2-methylpropanoate (Mal-trithiocarbonate) **5i**.

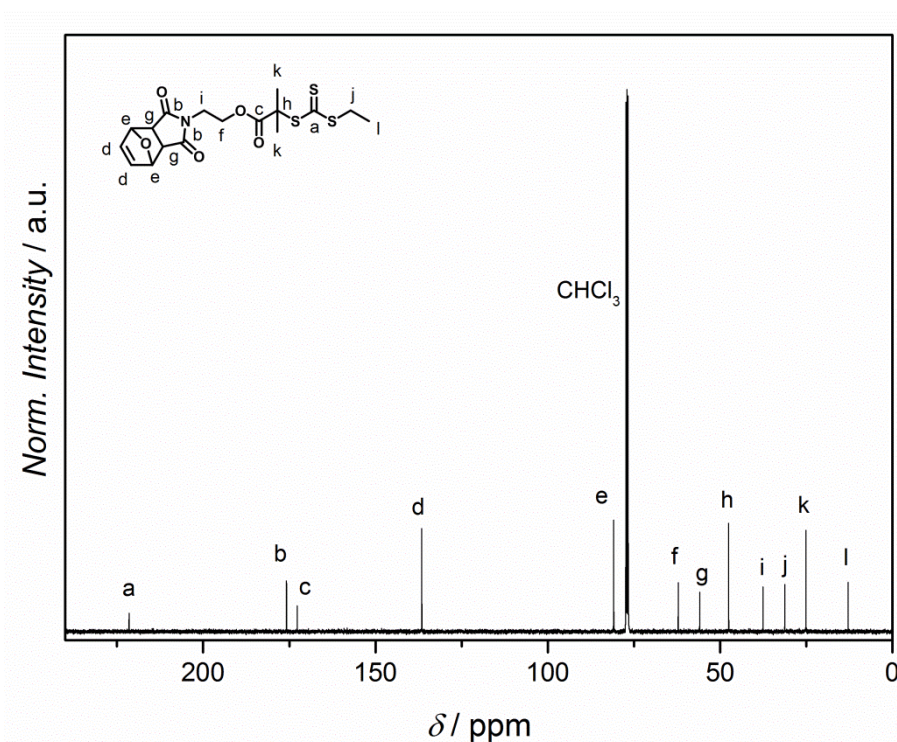
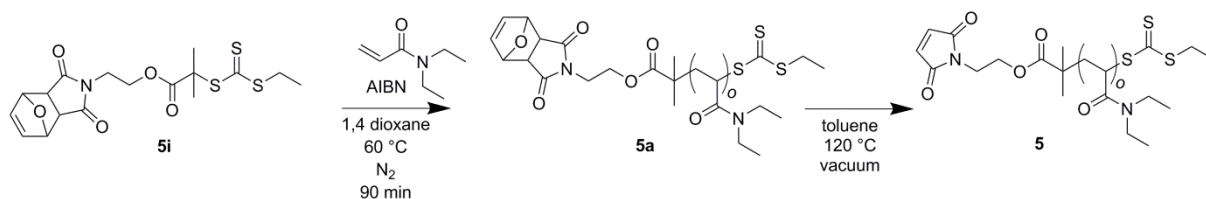
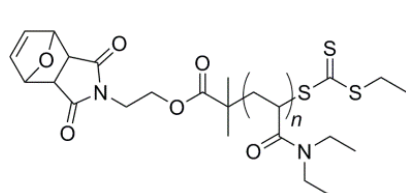


Figure S13. ^{13}C NMR spectrum (400 MHz, CDCl_3 , 25 °C) of 2-(1,3-dioxo-1,3,3a,4,7,7a-hexahydro-2H-4,7-epoxyisoindol-2-yl)ethyl 2-(((ethylthio)carbonothioyl)thio)-2-methylpropanoate (Mal-trithiocarbonate) **5i**.

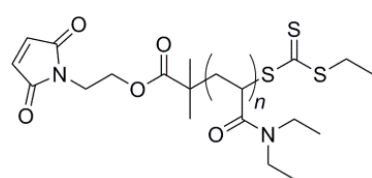


Scheme S2. Synthetic strategy for poly(DEAAm)-Mal **5**.



Synthesis of the protected maleimide functionalized poly(DEAAm) (poly(DEAAm)-Mal-protc.) (5a): DEAAm (1.00 g, 7.862 mmol, 114.67 eq.), Mal-trithiocarbonate (28.49 mg, 0.068 mmol, 1 eq.) and AIBN (1.13 mg, 0.006 mmol, 0.1 eq.) were placed in a Schlenk-tube and dissolved in 1,4-dioxane (1.10 mL).

Oxygen was removed from the solution via three freeze pump thaw cycles. The mixture was placed in preheated oil bath, stirred for 20 min at 60 °C and quenched by cooling on ice. The solution was dialyzed against deionized water with a SpectraPor3 membrane (MWCO = 1000 Da) for three days at 4 °C in the fridge and subsequently lyophilized. The product was obtained as slightly yellow powder (197.40 mg, $M_{n \text{ theo}} = 15000 \text{ g mol}^{-1}$, $M_{n \text{ SEC}} \text{ (DMAC)} = 5400 \text{ g mol}^{-1}$).



Deprotection of the maleimide functionalized poly(DEAAm) (poly(DEAAm)-Mal) (5): poly(DEAAm)-Mal-protc. **5a** was placed in a round bottom Schlenk-flask. The flask was heated to 120 °C in an oil bath overnight, while being evacuated under high vacuum.

Subsequently, the solid was dissolved in deionized water and lyophilized to result in a slightly orange powder (169.00 mg, $M_{n \text{ theo}} = 15000 \text{ g mol}^{-1}$, $M_{n \text{ SEC}} \text{ (DMAC)} = 5600 \text{ g mol}^{-1}$).

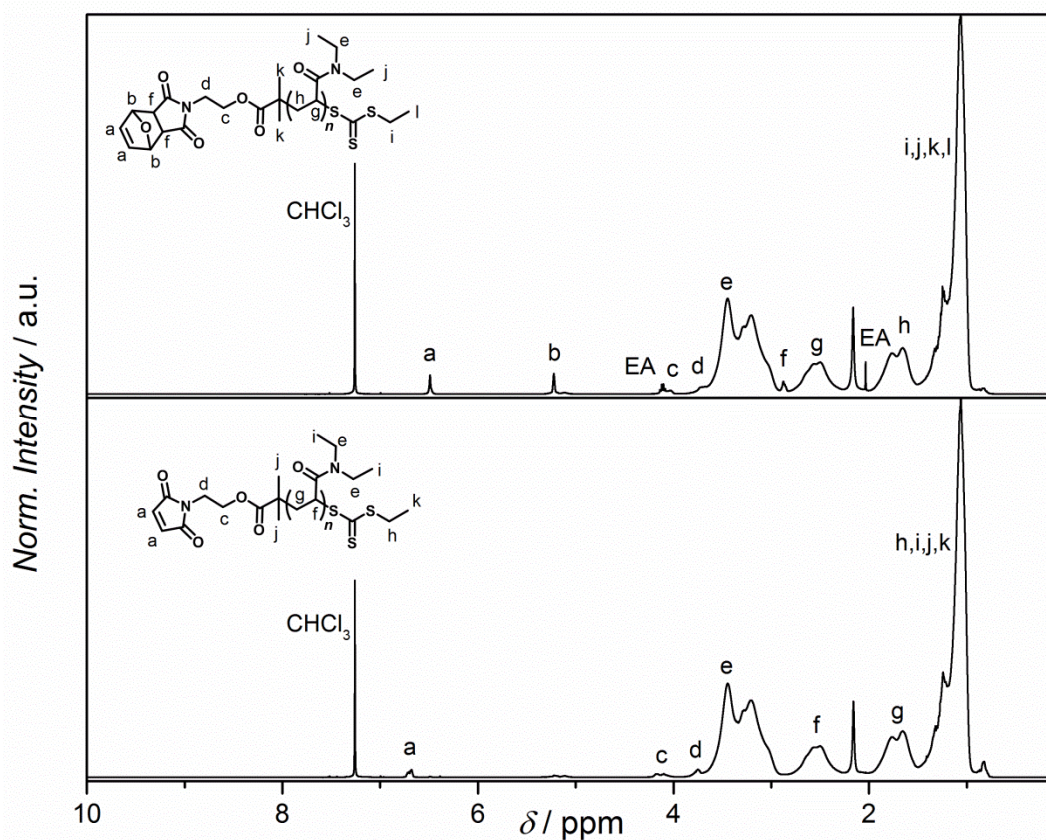


Figure S14. ^1H NMR spectra (400 MHz, CDCl_3 , 25 $^\circ\text{C}$) of poly(DEAAm)-Mal-protc. **5a** (above) and poly(DEAAm)-Mal **5**. The comparison of the two spectra shows the successful deprotection of the maleimide via the disappearance of the furan protection group resonances at 6.51 ppm (a) and 5.26 ppm (b). The appearance of the maleimide double bond resonances, in the spectrum on the bottom, at 6.71 ppm (a) also verifies the complete deprotection of **5a**.

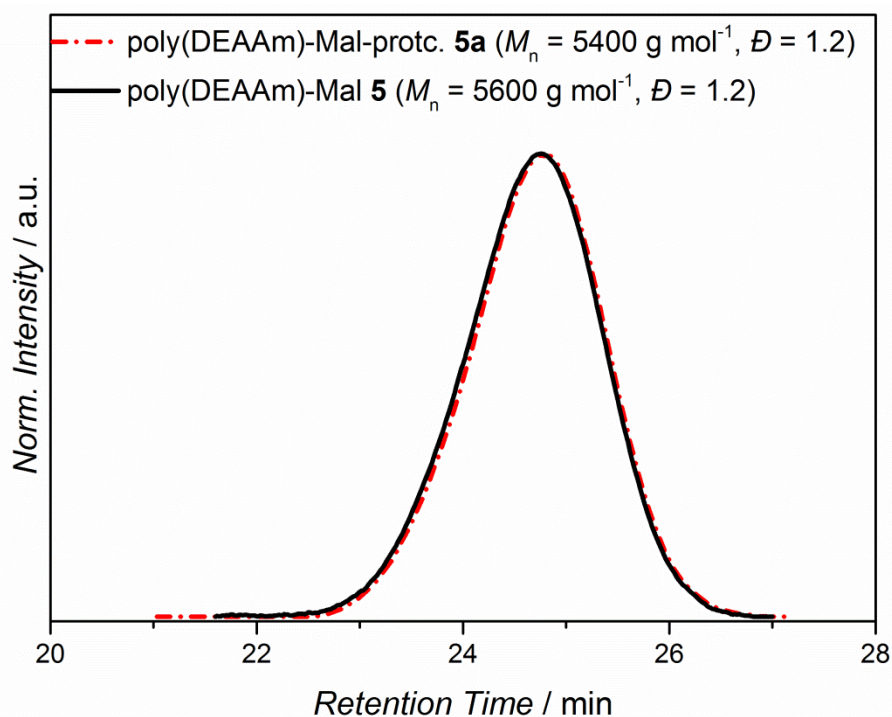


Figure S15. SEC traces of poly(DEAAm)-Mal-protc. **5a** (red) and poly(DEAAm)-Mal **5** (black) measured in DMAC at 50 $^\circ\text{C}$.

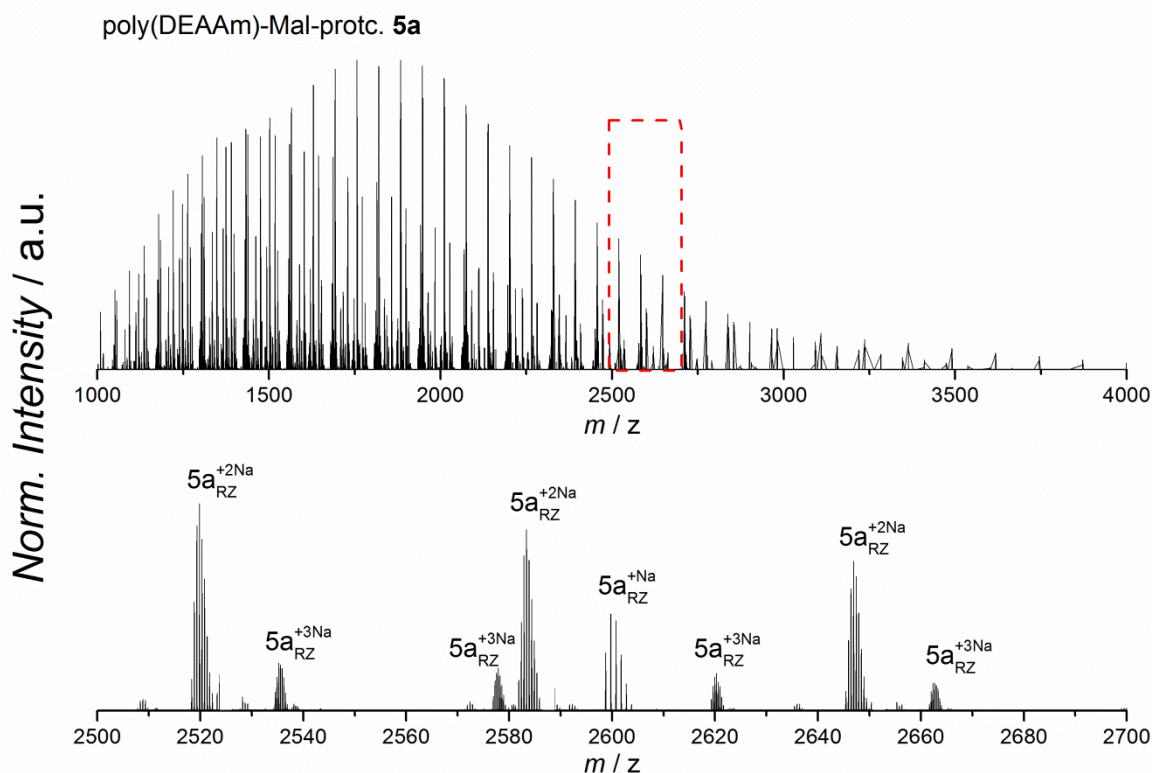


Figure S16. ESI-MS spectrum of poly(DEAAm)-Mal-protc. **5a** and a magnification of the spectrum (below). The spectrum shows the single, double and triple charged polymer chains of **5a** ionized with Na^+ .

Table S2. Mass peak assignment for poly(DEAAm)-Mal-protc. **5a**. Experimental and theoretical m/z values for the labelled peaks shown in **Figure S14**.

| m/z_{exp} | assignment | chemical formula | m/z_{theo} | $\Delta m/z$ |
|--------------------|-------------------------------------|--|---------------------|--------------|
| 2519.346 | p(DEAAm)-Mal-protc. + Na_2 | $[\text{C}_{269}\text{H}_{489}\text{N}_{37}\text{Na}_2\text{O}_{41}\text{S}_3]^{2+}$ | 2519.316 | 0.030 |
| 2535.566 | p(DEAAm)-Mal-protc. + Na_3 | $[\text{C}_{409}\text{H}_{749}\text{N}_{57}\text{Na}_3\text{O}_{61}\text{S}_3]^{3+}$ | 2535.542 | 0.024 |
| 2577.938 | p(DEAAm)-Mal-protc. + Na_3 | $[\text{C}_{416}\text{H}_{762}\text{N}_{58}\text{Na}_3\text{O}_{62}\text{S}_3]^{3+}$ | 2577.909 | 0.029 |
| 2583.399 | p(DEAAm)-Mal-protc. + Na_2 | $[\text{C}_{276}\text{H}_{502}\text{N}_{38}\text{Na}_2\text{O}_{42}\text{S}_3]^{2+}$ | 2583.368 | 0.031 |
| 2599.776 | p(DEAAm)-Mal-protc. + Na | $[\text{C}_{136}\text{H}_{242}\text{N}_{18}\text{NaO}_{22}\text{S}_3]^+$ | 2599.745 | 0.031 |
| 2619.973 | p(DEAAm)-Mal-protc. + Na_3 | $[\text{C}_{423}\text{H}_{775}\text{N}_{59}\text{Na}_3\text{O}_{63}\text{S}_3]^{3+}$ | 2619.941 | 0.032 |
| 2646.950 | p(DEAAm)-Mal-protc. + Na_2 | $[\text{C}_{283}\text{H}_{515}\text{N}_{39}\text{Na}_2\text{O}_{43}\text{S}_3]^{2+}$ | 2646.918 | 0.032 |
| 2662.672 | p(DEAAm)-Mal-protc. + Na_3 | $[\text{C}_{430}\text{H}_{788}\text{N}_{60}\text{Na}_3\text{O}_{64}\text{S}_3]^{3+}$ | 2662.642 | 0.030 |

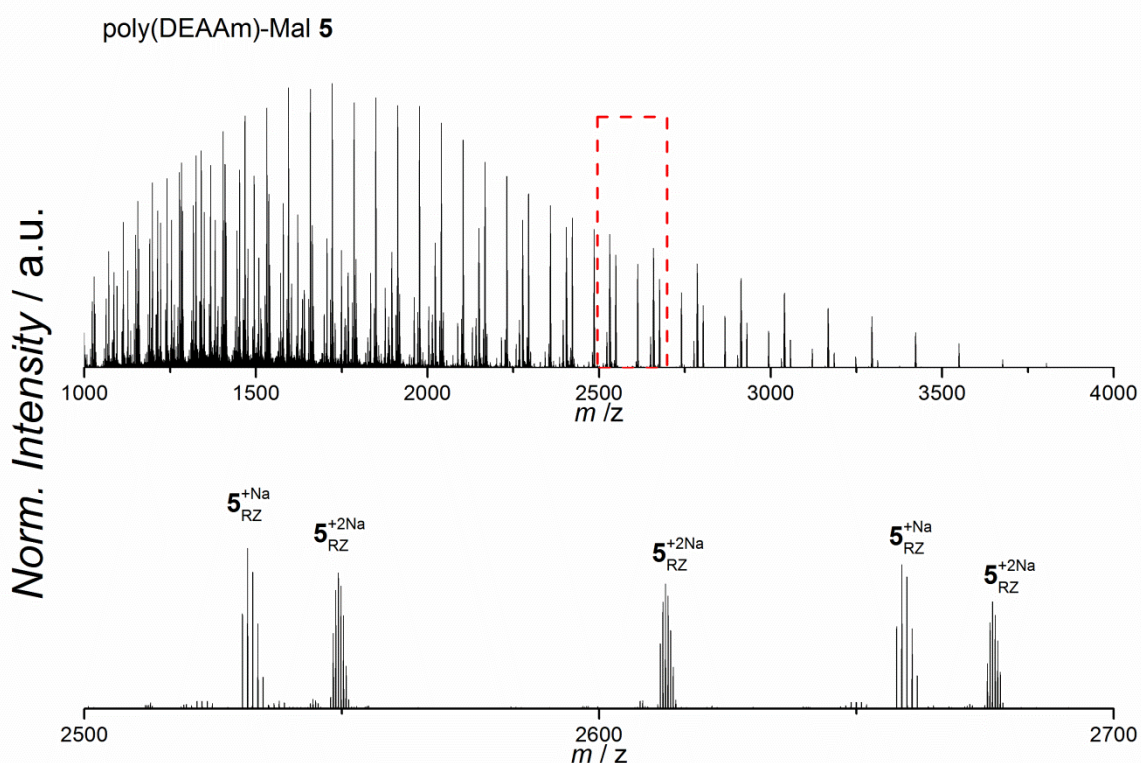
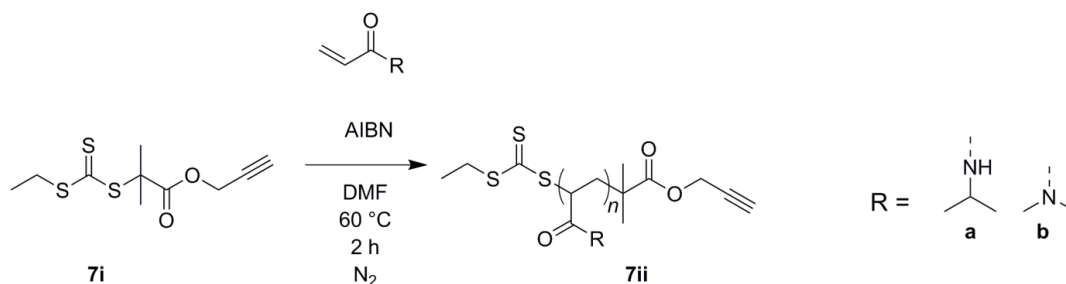


Figure S17. ESI-MS spectrum of poly(DEAAm)-Mal **5** and a magnification of the spectrum (below). The spectrum shows the single and double charged polymer chains of **5** ionized with Na^+ .

Table S3. Mass peak assignment for poly(DEAAm)-Mal **5**. Experimental and theoretical m/z values for the labelled peaks shown in **Figure S15**.

| m/z_{exp} | assignment | chemical formula | m/z_{theo} | $\Delta m/z$ |
|--------------------|------------------------------|--|---------------------|--------------|
| 2531.732 | p(DEAAm)-Mal + Na | $[\text{C}_{132}\text{H}_{238}\text{N}_{18}\text{NaO}_{21}\text{S}_3]^+$ | 2531.719 | 0.013 |
| 2549.365 | p(DEAAm)-Mal + Na_2 | $[\text{C}_{272}\text{H}_{498}\text{N}_{38}\text{Na}_2\text{O}_{41}\text{S}_3]^{2+}$ | 2549.355 | 0.01 |
| 2612.915 | p(DEAAm)-Mal + Na_2 | $[\text{C}_{279}\text{H}_{511}\text{N}_{39}\text{Na}_2\text{O}_{42}\text{S}_3]^{2+}$ | 2612.905 | 0.01 |
| 2658.832 | p(DEAAm)-Mal + Na | $[\text{C}_{139}\text{H}_{251}\text{N}_{19}\text{NaO}_{22}\text{S}_3]^+$ | 2658.819 | 0.013 |
| 2676.467 | p(DEAAm)-Mal + Na_2 | $[\text{C}_{286}\text{H}_{524}\text{N}_{40}\text{Na}_2\text{O}_{43}\text{S}_3]^{2+}$ | 2676.454 | 0.013 |

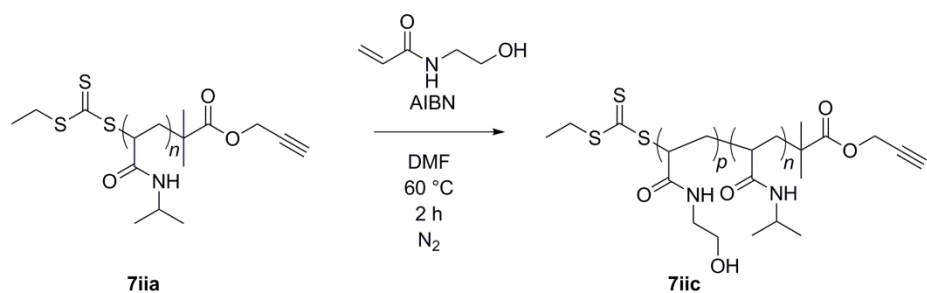


Scheme S3. Synthetic strategy for the alkyne-functionalized polymer blocks: poly(NiPAAm)-alkyne **7iia** and poly(DMAAm)-alkyne **7iib**.

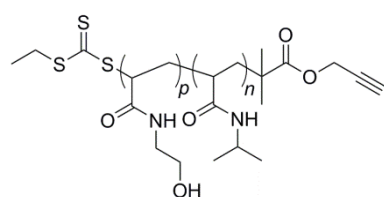
Synthesis of alkyne functionalized polymer poly(NiPAAm) (7iia): In a Schlenk-tube NiPAAm (5.00 g, 44.19 mmol, 87.00 eq., 1921.10 mmol L⁻¹), AIBN (0.008 g, 0.05 mmol, 0.1 eq., 2.11 mmol L⁻¹) and prop-2-yn-1-yl 2-(((ethylthio)carbonothioyl)thio)-2-methylpropanoate **7i** (0.135 g, 0.51 mmol, 1.0 eq., 22.08 mmol L⁻¹) were dissolved in DMF (23 mL) and equipped with a stirring bar. Via three freeze-pump-thaw cycles, oxygen was removed from the reaction mixture and the tube was placed in a preheated oil bath at 60 °C. After 2.5 h the reaction was quenched by cooling with liquid nitrogen and subsequently dialyzed against deionized water (SpectraPor3 membrane (MWCO = 1000 Da)) for three days at 4 °C in the fridge. The water was removed by lyophilization and the polymer was obtained as a yellow solid (1.03 g, $M_{n \text{ theo}} = 10500 \text{ g mol}^{-1}$, $M_{n \text{ SEC}}(\text{DMAC}) = 8800 \text{ g mol}^{-1}$, $\mathcal{D} = 1.1$).

Table S4. Reaction conditions for the CTA **7i** mediated polymerization of DMAAm. The same synthesis procedures apply as it was described for poly(NiPAAm)-alkyne **7iia** above. The reaction proceeded at 60 °C for 2 h. c_{Mon}^0 is the concentration of the monomer, c_{CTA}^0 is the concentration of CTA **7i** and c_{AIBN}^0 is the initial AIBN concentration. $M_{n \text{ theo}}$ refers to the calculated number average molecular weight based on 100% conversion.

| Polymer | c_{Mon}^0 [mmol L ⁻¹] | c_{CTA}^0 [mmol L ⁻¹] | c_{AIBN}^0 [mmol L ⁻¹] | $M_{n \text{ theo}}$ [g mol ⁻¹] | $M_{n \text{ SEC}}$ [g mol ⁻¹] | \mathcal{D} |
|----------------------|---|---|--|--|---|---------------|
| p(DMAAm) 7iib | 3362.50 | 21.94 | 2.19 | 15400 | 10100 | 1.1 |



Scheme S4. Chain extension of poly(NiPAAm)-alkyne **7iia** with HOEAAM.



Chain extension poly(NiPAAm)-alkyne 7iic: Poly(NiPAAm)-alkyne **7iia** (M_n SEC (DMAC) = 8800 g mol⁻¹, 1.00 g, 0.11 mmol, 1.0 eq., 2.84 mmol L⁻¹), AIBN (0.004 g, 0.02 mmol, 0.21 eq., 0.61 mmol L⁻¹) and HOEAAM (2.00 g,

17.37 mmol, 152.87 eq., 434.29 mmol L⁻¹) were placed in a Schlenk-tube and dissolved in DMF (40 mL). Oxygen was removed from the reaction mixture via three freeze-pump-thaw cycles and the tube was subsequently placed in an oil bath at 60 °C. The solution was stirred at 60 °C for 2.5 h and quenched by cooling with liquid nitrogen. The mixture was dialyzed against deionized water for three days with a SpectraPor3 membrane (MWCO = 1000 Da). After lyophilization the product was obtained as yellow powder (1.03 g, M_n SEC (DMAC) = 14600 g mol⁻¹, \bar{D} = 1.1).

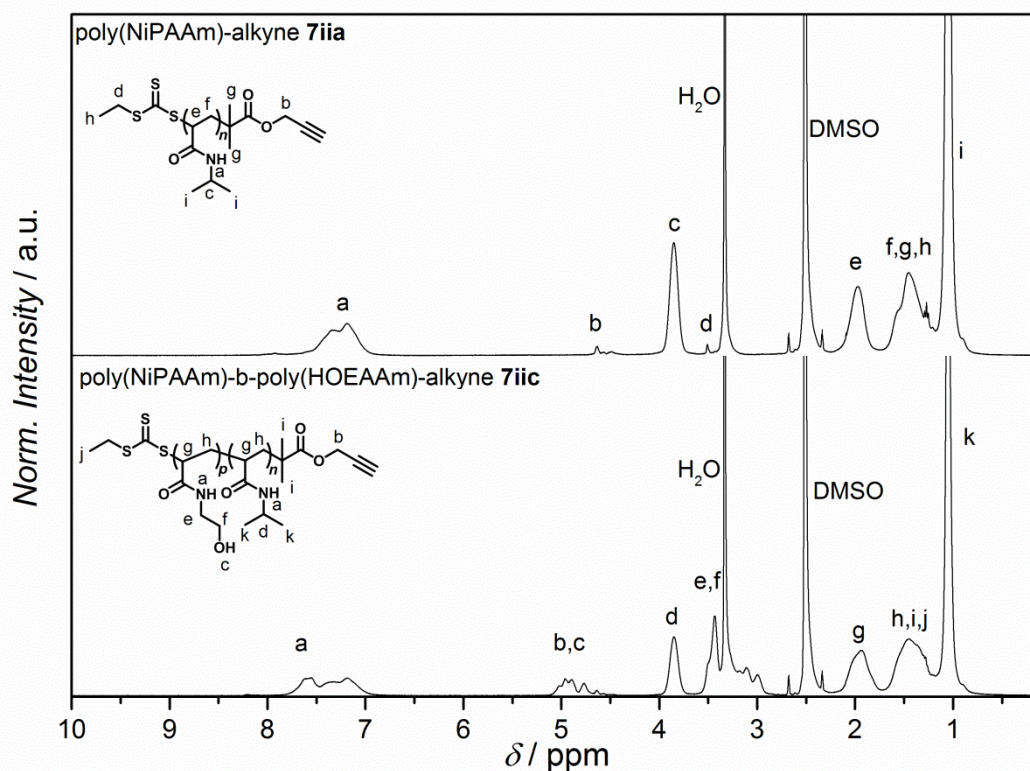


Figure S18. ^1H NMR spectrum (400 MHz, $\text{DMSO-}d_6$, $25\text{ }^\circ\text{C}$) of poly(NiPAAm)-alkyne **7iia** above and poly(NiPAAm)-*b*-poly(HOEAAM)-alkyne **7iic** after the chain extension of **7iia**.

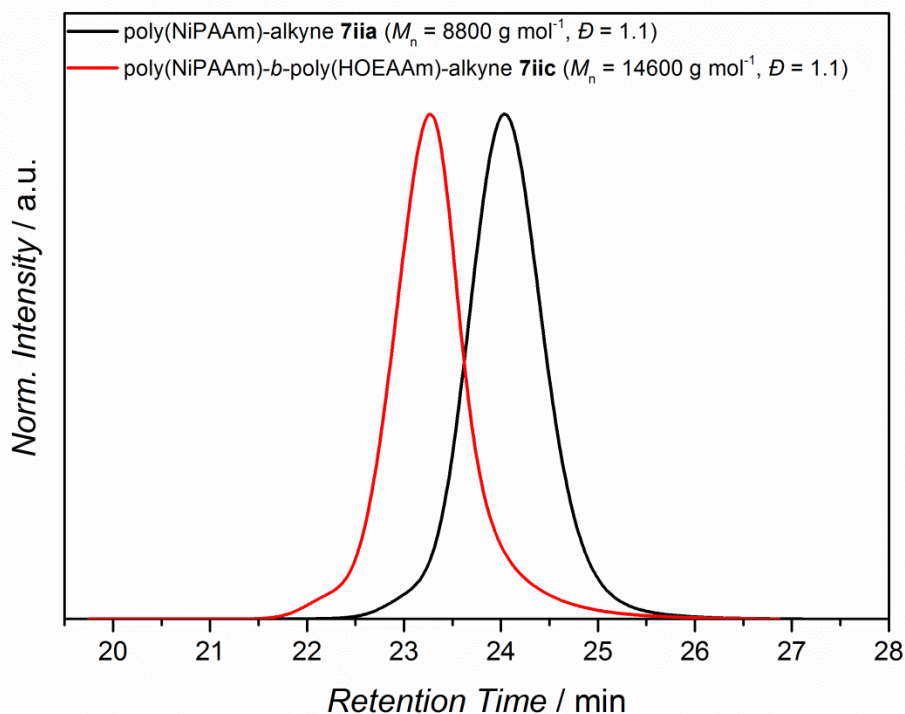
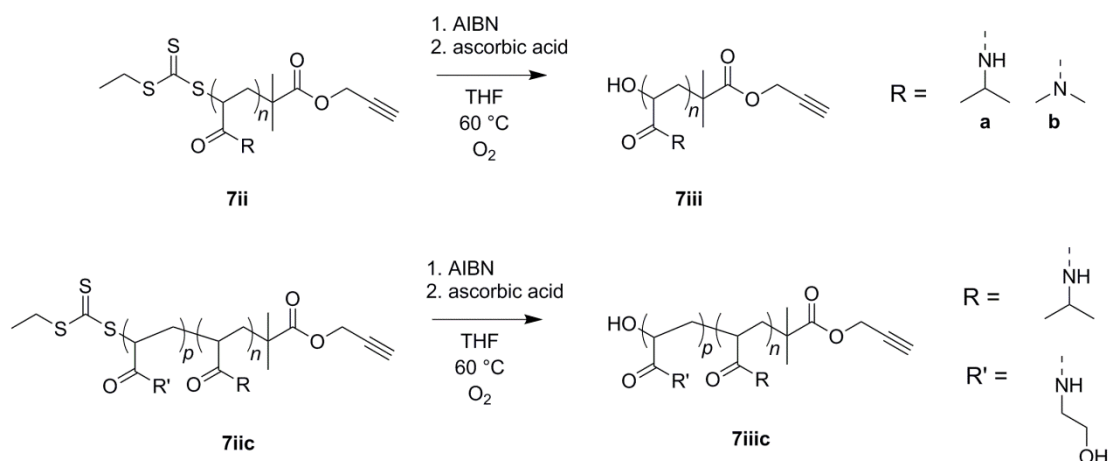
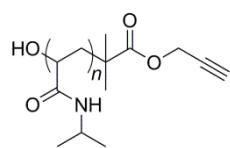


Figure S19. SEC traces of before (black) and after (red) the chain extension of poly(NiPAAm)-alkyne **7iia** with HOEAAM, resulting in poly(NiPAAm)-*b*-poly(HOEAAM)-alkyne **7iic** (red). The SEC traces were measured in DMAC at $50\text{ }^\circ\text{C}$.



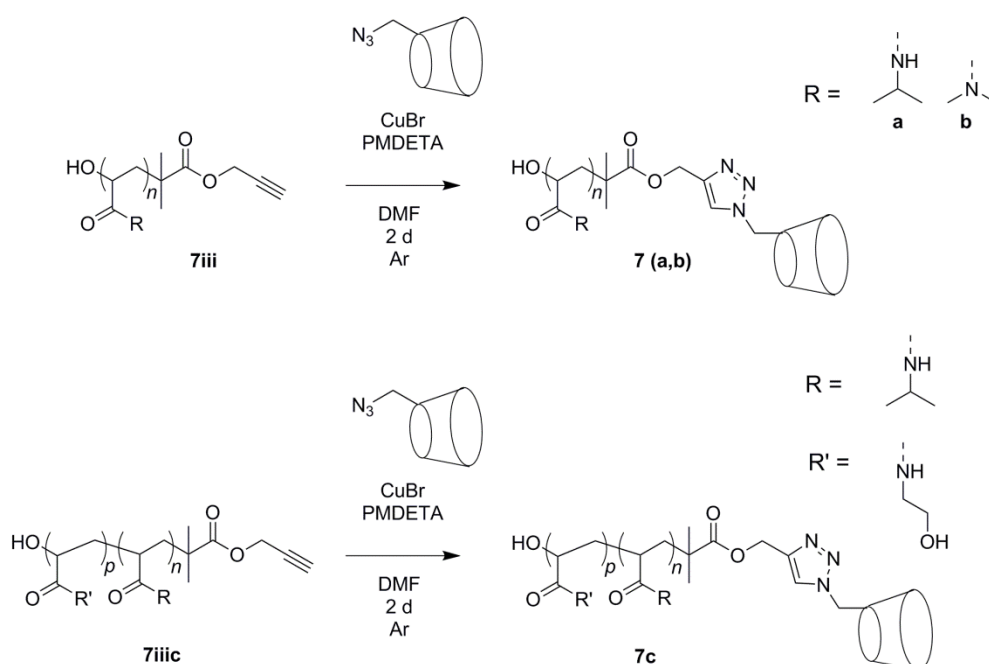
Scheme S5. Synthetic strategy for the alkyne-functionalized polymer hydroxyl terminated blocks: alkyne-poly(NiPAAm)-OH **7iiia**, alkyne-poly(DMAAm)-OH **7iiib** and alkyne-poly(NiPAAm)-*b*-poly(HOEAAm)-OH **7iiic**.



Synthesis of hydroxyl terminated, alkyne functionalized poly(NiPAAm) (alkyne-poly(NiPAAm)-OH) (7iiia): In a round bottom flask freshly distilled THF (52 mL) was heated to 60 °C in an oil bath. Under vigorous stirring AIBN (340 mg, 2.07 mmol, 36.00 eq., 39.81 mmol L⁻¹) was added to the flask and stirred for 5 min. Subsequently, poly(NiPAAm)-alkyne **7iia** (M_n (DMAC) = 8800 g mol⁻¹, 500 mg, 0.06 mmol, 1.00 eq., 1.96 mmol L⁻¹) was added to the mixture which turned light yellow. The solution was stirred until complete discoloration (indication of full conversion) under ambient oxygen. To quench the generated peroxides, the temperature was reduced to 40 °C and ascorbic acid (108 mg, 0.61 mmol, 6.0 eq., 5.68 mmol L⁻¹) was added. Peroxide dipsticks (Quantofix Peroxid 100, 1 – 100 mg L⁻¹ H₂O₂) were employed to check for the presence of peroxides. The solvent was reduced in vacuo after the removal of the peroxides and the residue was dialyzed against deionized water for three days, employing a SpectraPor3 membrane (MWCO = 1000 Da). The product was obtained as white powder (414.00 mg, M_n SEC (DMAC) = 8900 g mol⁻¹, $D = 1.1$).

Table S5. Reaction conditions for the radical transformation reactions of the trithiocarbonate into a hydroxyl function for poly(DMAAm)-alkyne **7iib** and poly(NiPAAm)-*b*-(HOEAAM)-alkyne **7iic**. The same synthetic procedure applies as for poly(NiPAAm)-alkyne **7iia** above. c_{Polymer}^0 is the concentration of the polymer, c_{AIBN}^0 is the initial AIBN concentration and $c_{\text{ascorbic acid}}^0$ is the concentration of the radical quencher (ascorbic acid).

| Polymer | M_n [g mol ⁻¹] | c_{Polymer}^0 [mmol L ⁻¹] | c_{AIBN}^0 [mmol L ⁻¹] | $c_{\text{ascorbic acid}}^0$ [mmol L ⁻¹] | M_n SEC [g mol ⁻¹] | \mathcal{D} |
|--|---------------------------------|---|--|---|-------------------------------------|---------------|
| p(DMAAm) 7iib | 10100 | 1.99 | 39.60 | 11.80 | 11700 | 1.3 |
| p(NiPAAm)- <i>b</i> - p(HOEAAM) 7iic | 14600 | 1.04 | 39.31 | 11.87 | 15500 | 1.3 |



Scheme S6. Synthetic strategy for the CuAAC-click reaction of an azide-functionalized β -CD with the alkyne functionalized polymers: alkyne-poly(NiPAAm)-OH **7iia**, alkyne-poly(DMAAm)-OH **7iib** and the diblock copolymer alkyne-poly(NiPAAm)-*b*-poly(HOEAAM)-OH **7iic**.

Synthesis of β -cyclodextrin functionalized poly(NiPAAm) (poly(NiPAAm)- β -CD) (7a): In a Schlenk-tube *N,N,N',N',N''*-pentamethyldiethylenetriamine (PMDETA) (100 mg, 0.61 mmol, 14.90 eq., 26.45 mmol L⁻¹), alkyne-poly(NiPAAm)-OH **7iia** (M_n SEC = 8900 g mol⁻¹, 200 mg, 0.06 mmol, 1.00 eq., 1.77 mmol L⁻¹) and β -CD-N₃ **4** (485 mg, 0.42 mmol, 10.00 eq., 18.23 mmol L⁻¹) were dissolved in DMF (23 mL). Oxygen was removed from the reaction mixture via three freeze pump thaw cycles and CuBr (77 mg,

0.54 mmol, 13.15 eq., 23.34 mmol L⁻¹) was added under a stream of argon. The mixture was stirred for two days at ambient temperature und dialyzed against deionized water (SpectraPor3 membrane (MWCO = 1000 Da)) for three days. After lyophilization, the product was obtained as white solid (189 mg, M_n SEC (DMAC) = 8800 g mol⁻¹, \bar{D} = 1.2).

Table S6. Reaction conditions for the CuAAC-click reactions of an azide-functionalized β -CD to alkyne terminated polymers as was described above for alkyne-poly(NiPAAm)-OH **7iia**. c^0_{Polymer} is the concentration of the polymer, $c^0_{\beta\text{-CD-azide}}$ is the concentration of the azide-functionalized β -CD, c^0_{CuBr} is the concentration of CuBr and c^0_{PMDETA} the concentration of the ligand.

| Polymer | M_n [g mol ⁻¹] | c^0_{Polymer} [mmol L ⁻¹] | $c^0_{\beta\text{-CD-azide}}$ [mmol L ⁻¹] | c^0_{CuBr} [mmol L ⁻¹] | c^0_{PMDETA} [mmol L ⁻¹] | M_n SEC [g mol ⁻¹] | \bar{D} |
|--|---------------------------------|---|--|--|--|-------------------------------------|-----------|
| p(DMAAm) 7b | 11700 | 1.25 | 37.29 | 26.04 | 23.96 | 10700 | 1.3 |
| p(NiPAAm)- <i>b</i> - p(HOEAAM) 7c | 15500 | 0.86 | 17.75 | 22.77 | 25.86 | 16400 | 1.3 |

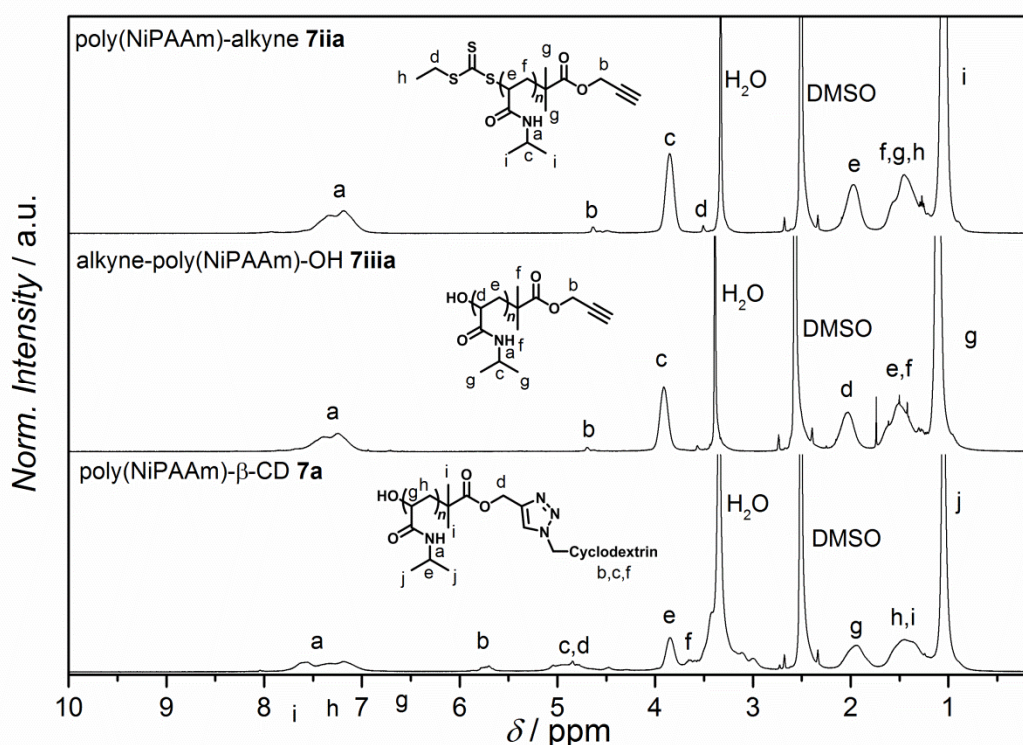


Figure S20. ¹H NMR spectrum (400 MHz, DMSO-*d*₆, 25 °C) of poly(NiPAAm)-alkyne **7iia** above, alkyne-poly(NiPAAm)-OH **7iia** and the final β -CD functionalized poly(NiPAAm)- β -CD **7a**, clearly showing the proton resonance signals of β -CD.

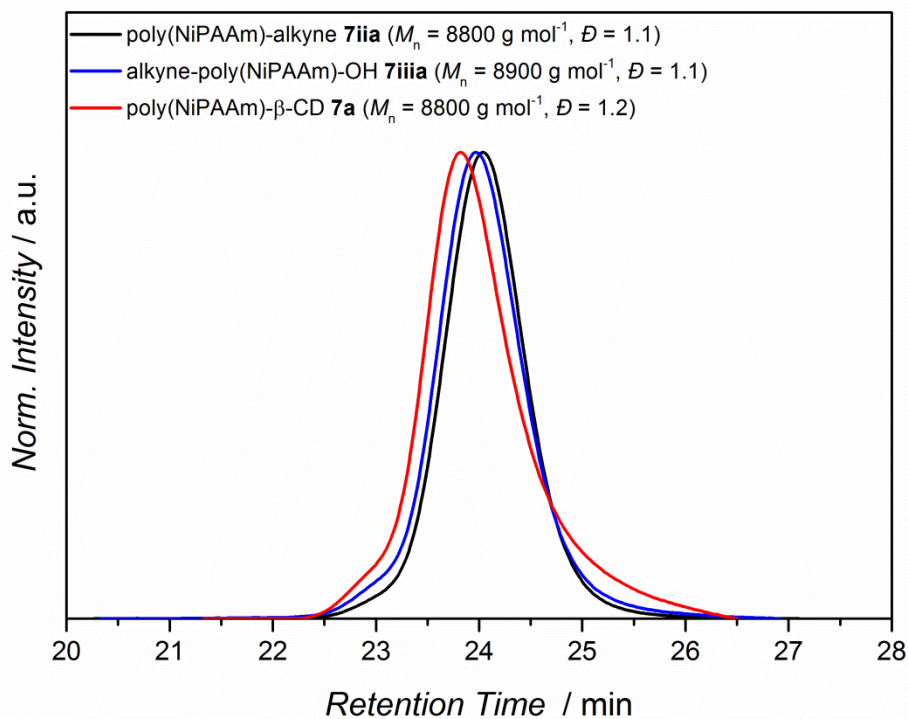


Figure S21. SEC traces of poly(NiPAAm)-alkyne **7iia** (black), alkyne-poly(NiPAAm)-OH **7iiaa** (blue) and poly(NiPAAm)- β -CD **7a** (red) measured in DMAC at 50 °C.

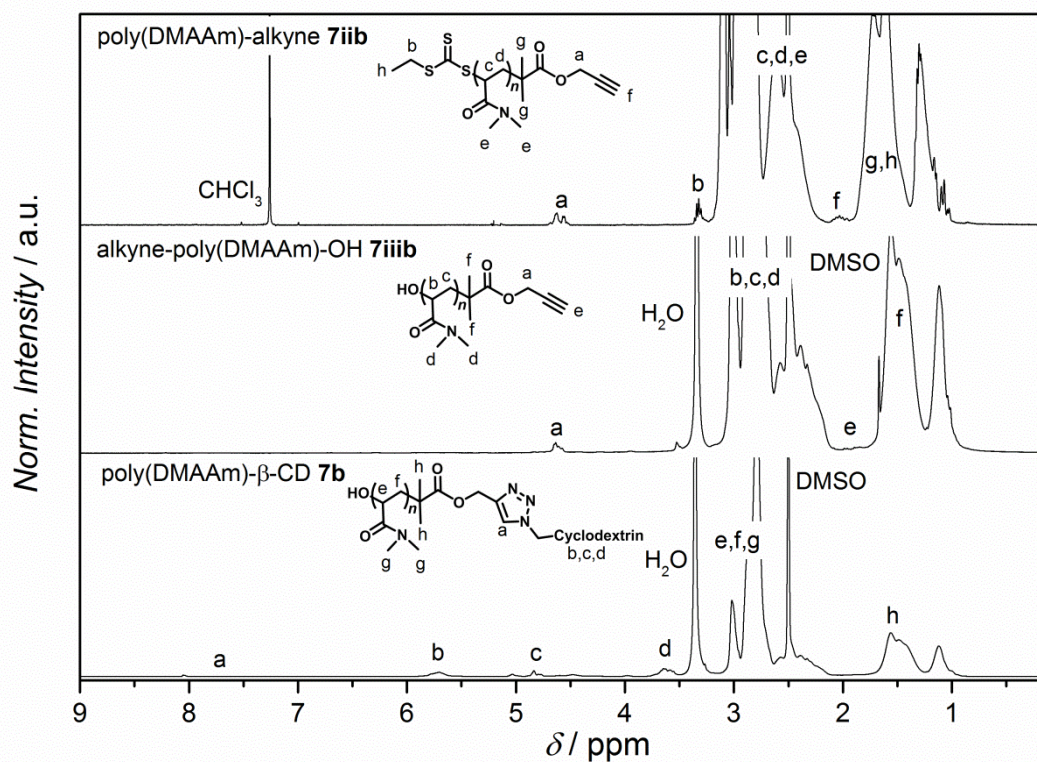


Figure S22. ^1H NMR spectrum (400 MHz, CDCl_3 and $\text{DMSO-}d_6$, 25 °C) of poly(DMAAm)-alkyne **7iib** above, alkyne-poly(DMAAm)-OH **7iibb** and the final β -CD-functionalized poly(DMAAm)- β -CD **7b**, clearly showing the proton resonances of β -CD.

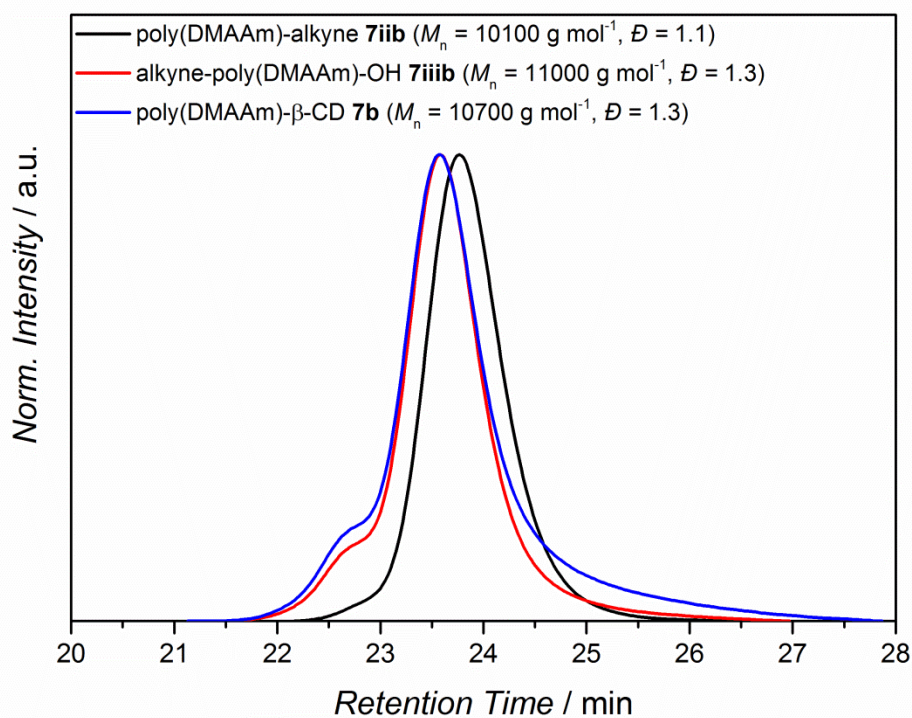


Figure S23. SEC traces of poly(DMAAm)-alkyne **7iib** (black), alkyne-poly(DMAAm)-OH **7iiib** (red) and poly(DMAAm)- β -CD **7b** (blue) measured in DMAC at 50 °C.

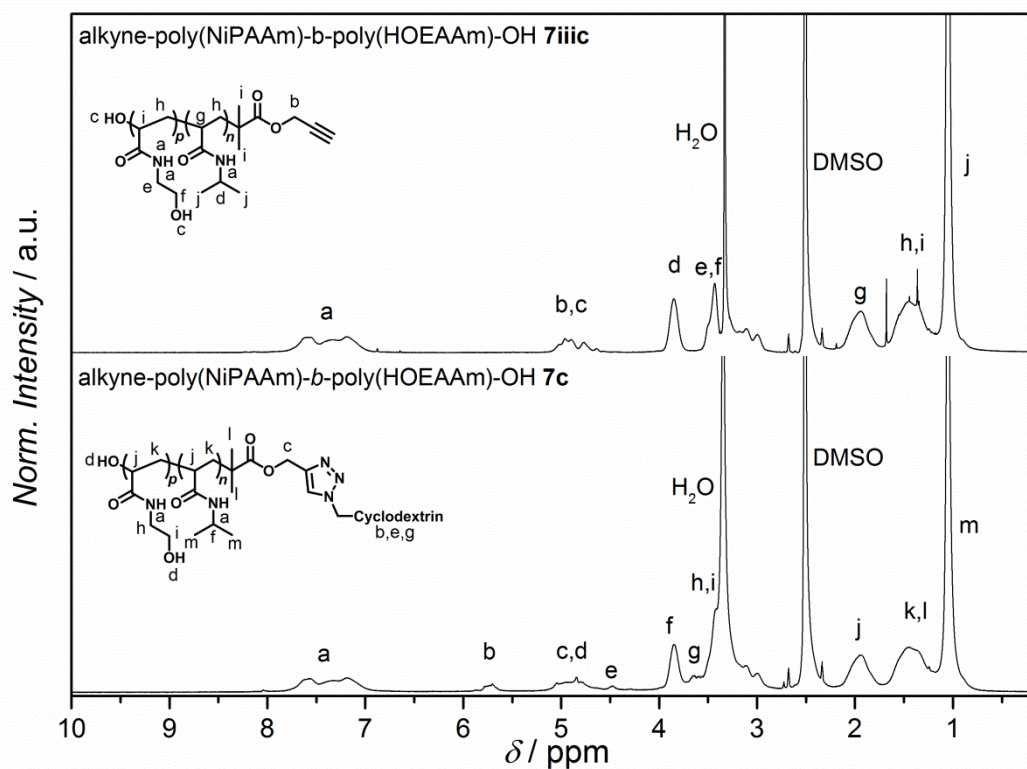


Figure S24. ^1H NMR spectrum (400 MHz, $\text{DMSO-}d_6$, 25 °C) of alkyne-poly(NiPAAm)-*b*-poly(HOEAAM)-OH **7iiic** above and the final β -CD functionalized poly(NiPAAm)- β -CD **7c** below, clearly showing the proton resonances of β -CD.

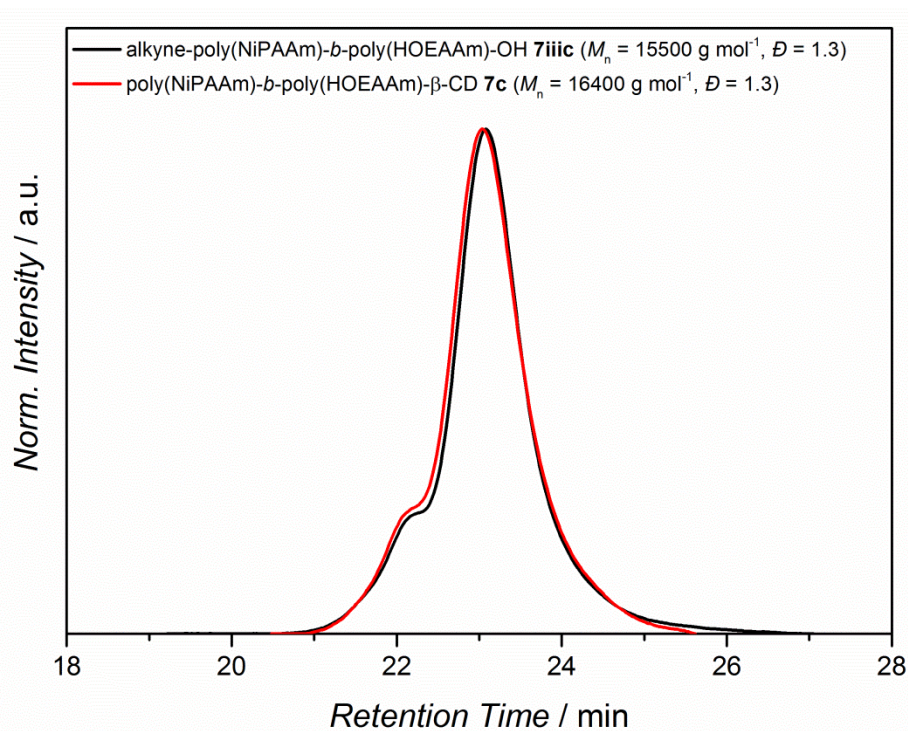


Figure S25. SEC traces of alkyne-poly(NiPAAm)-*b*-poly(HOEAAM)-OH **7iiiic** (black) and poly(NiPAAm)-*b*-(HOEAAM)- β -CD **7c** (red) measured in DMAC at 50 °C.

Theoretical molecular weight calculations

Theoretical molecular weights were calculated with the equation below:

$$M_{n \text{ theo}} = \left(\frac{[\text{monomer}]}{[\text{CTA}]_0} \times M_{\text{monomer}} \times U \right) + M_{\text{CTA}}$$

Formation of the diblock copolymer via the photo-induced Diels-Alder reaction: poly(DEAAm)-Mal (20.00 mg, 0.0014 mmol, 1.0 eq. based on M_n SEC = 5600 g mol⁻¹) and poly(DMAAm)-*t*BuBnPE (10.43 mg, 0.0035 mmol, 0.4 eq. based on M_n SEC = 7300 g mol⁻¹) were dissolved in MeCN (6 mL) and aliquoted into headspace vials. The vials were crimped airtight with SBR seals with PTFE inlet and oxygen was removed from the solution by purging with nitrogen for 15 min. Subsequently, the vial was placed in a custom-built photoreactor and irradiated at a wavelength of 320 nm for 40 min. The solvent was removed in vacuo and the residue measured directly in the SEC (30.00 mg, M_n SEC (DMAC) = 10000 g mol⁻¹).

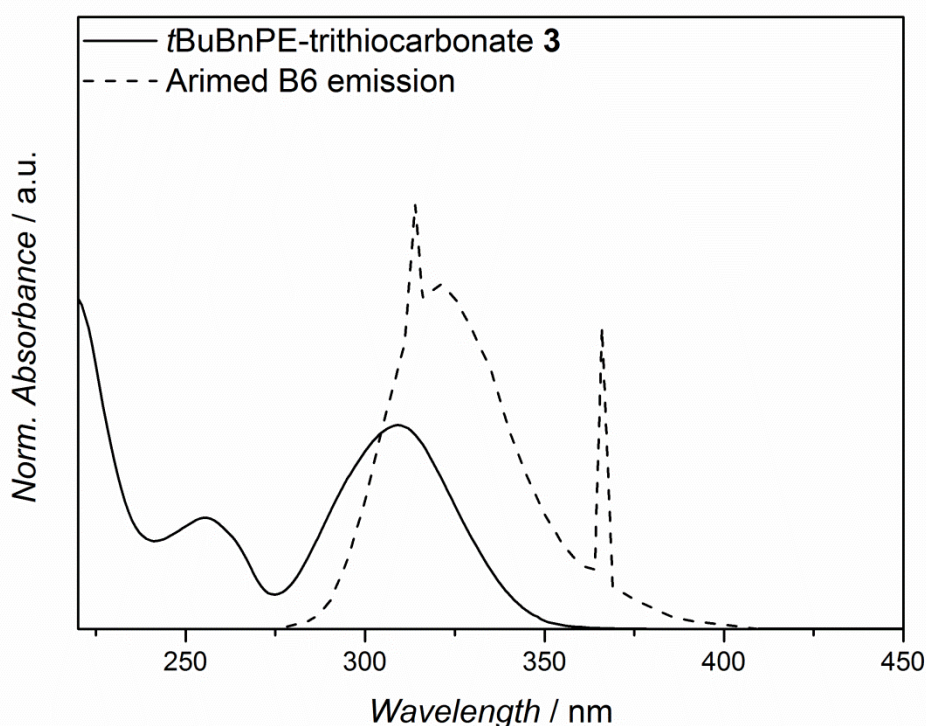


Figure S26. Emission spectrum of the employed compact low-pressure fluorescent lamp (Arimed B6, 36 W) and the UV-Vis spectrum of the *t*BuBnPE-trithiocarbonate RAFT agent (**3**) measured in MeCN.

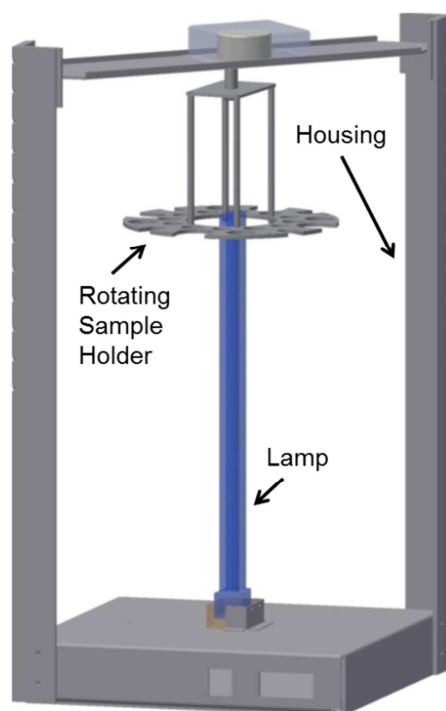


Figure S 27. Illustration of the custom-built photoreactor employed in the current study.

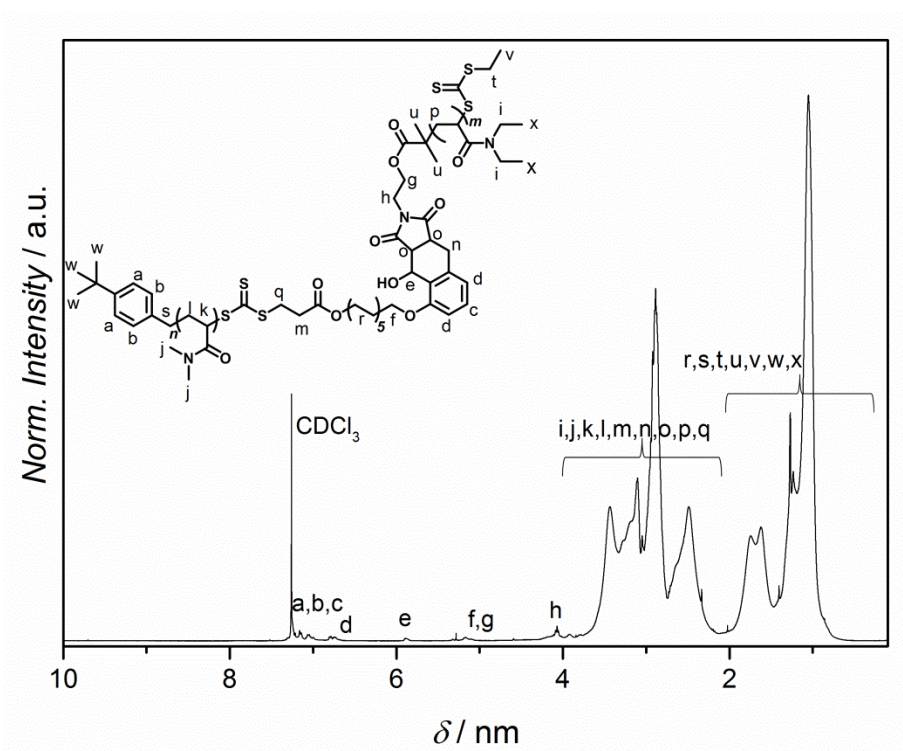


Figure S28. ^1H NMR spectrum (400 MHz, CDCl_3) of the diblock copolymer **6**.

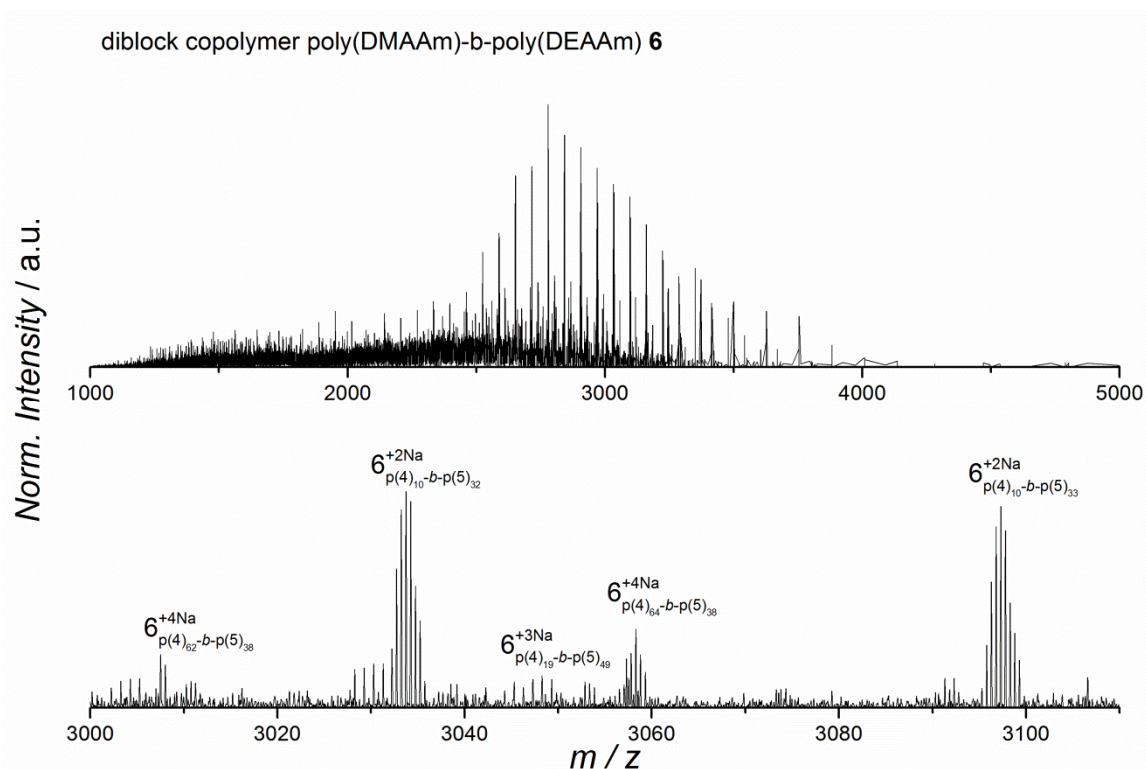


Figure S29. ESI-MS spectrum of poly(DMAAm)-*b*-poly(DEAAm) **6** and a magnification of the spectrum (below). The spectrum shows the double, triple and quadruple charged polymer chains of **6** ionized with Na⁺. *We note that $\Delta m/z$ is very high and outside the resolution of our Orbitrap mass analyzer. The analyzed structure is a highly complex diblock copolymer and we assume that during ionization, for example, proton abstraction or similar processes occur. We also note that the assigned peaks do not correspond to the single polymer blocks (**4** and **5**). On balance all analytical evidence (SEC, NMR and DLS) clearly points to the formation of the diblock copolymer **6** and that the sub-Da deviation occurs during the ionization process.

Table 7. Mass peak assignment for poly(DMAAm)-*b*-poly(DEAAm) **6**. Experimental and theoretical m/z values for the labelled peaks shown in **Figure S21**.

| m/z_{exp} | assignment | chemical formula | m/z_{theo} | $\Delta m/z^*$ |
|--------------------|--|--|---------------------|----------------|
| 3007.499 | p(DMAAm) ₆₂ -b-p(DEAAm) ₃₈ + Na ₄ | [C ₆₂₃ H ₁₁₁₇ N ₁₀₁ Na ₄ O ₁₀₈ S ₆] ⁴⁺ | 3006.822 | 0.677 |
| 3033.731 | p(DMAAm) ₁₀ -b-p(DEAAm) ₃₂ + Na ₂ | [C ₃₂₁ H ₅₇₁ N ₄₃ Na ₂ O ₅₀ S ₆] ²⁺ | 3033.575 | 0.156 |
| 3047.275 | p(DMAAm) ₁₉ -b-p(DEAAm) ₄₉ + Na ₃ | [C ₄₈₅ H ₈₇₃ N ₆₉ Na ₃ O ₇₆ S ₆] ³⁺ | 3047.483 | 0.208 |
| 3057.782 | p(DMAAm) ₆₄ -b-p(DEAAm) ₃₈ + Na ₄ | [C ₆₂₉ H ₁₁₂₅ N ₁₀₅ Na ₄ O ₁₁₂ S ₆] ⁺ | 3056.836 | 0.946 |
| 3097.281 | p(DMAAm) ₁₀ -b-p(DEAAm) ₃₃ + Na ₂ | [C ₃₂₈ H ₅₈₄ N ₄₄ Na ₂ O ₅₁ S ₆] ²⁺ | 3097.125 | 0.156 |

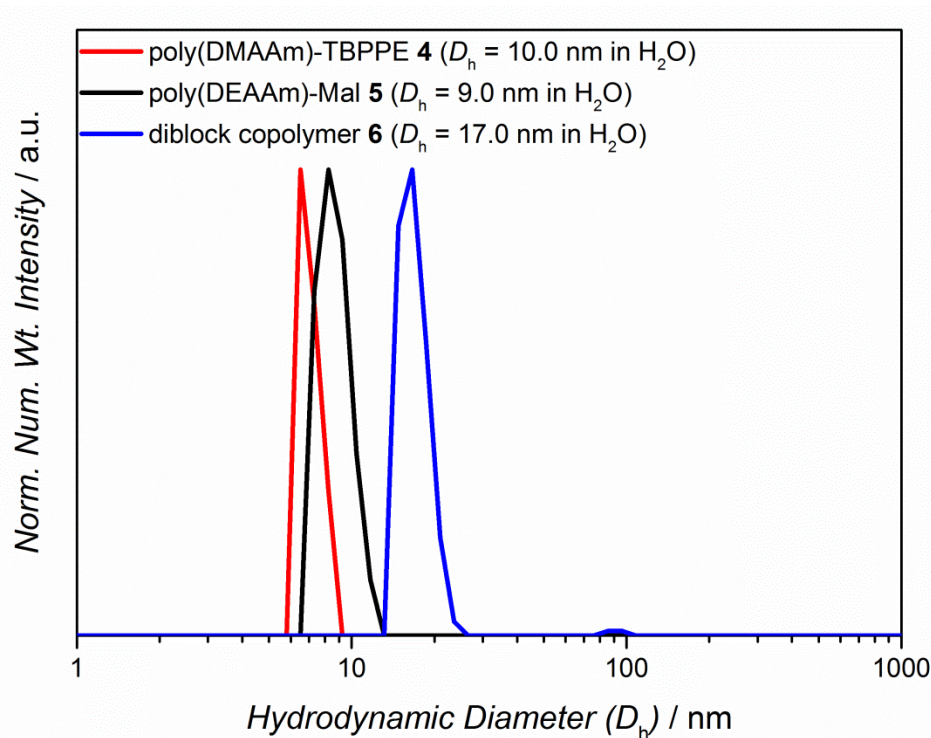


Figure S30. DLS measurements at 25 °C in Milli Q water, showing number weighted size distributions of the single blocks: poly(DEAAm)-Mal **5** and poly(DMAAm)-*t*BuBnPE **4**, as well as the diblock copolymer **6**. The samples were measured at a concentration of 0.06 mmol L⁻¹. The corresponding autocorrelation functions are listed below.

DLS autocorrelation functions:

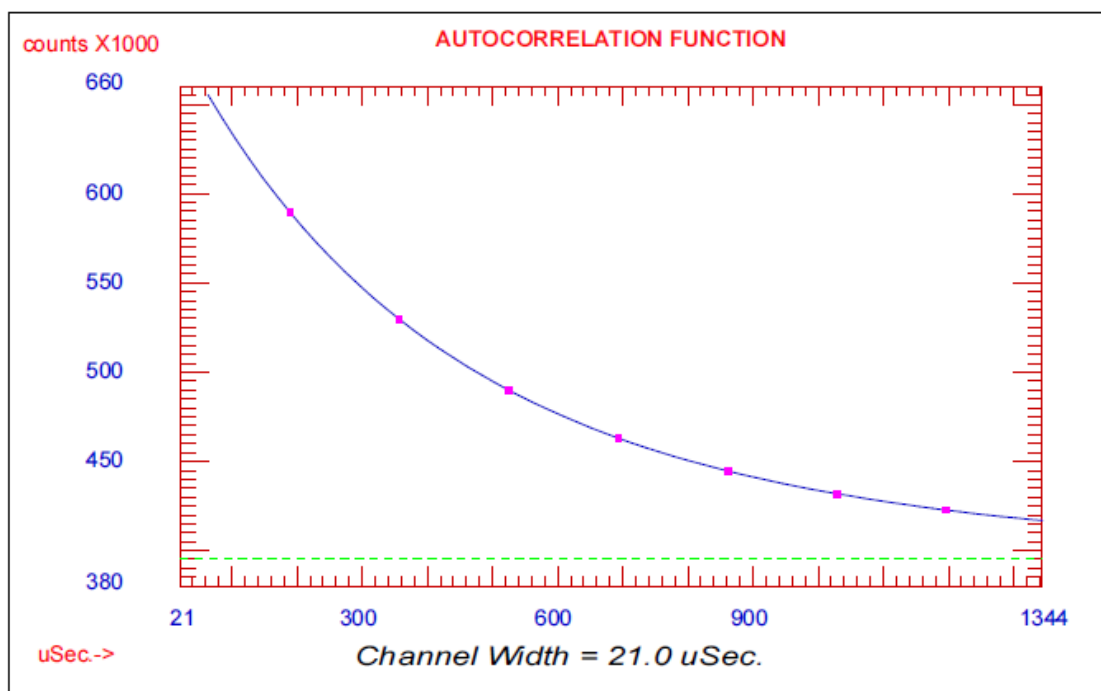


Figure S31. Autocorrelation function of the DLS measurement of poly(DEAAm)-Mal **5**.

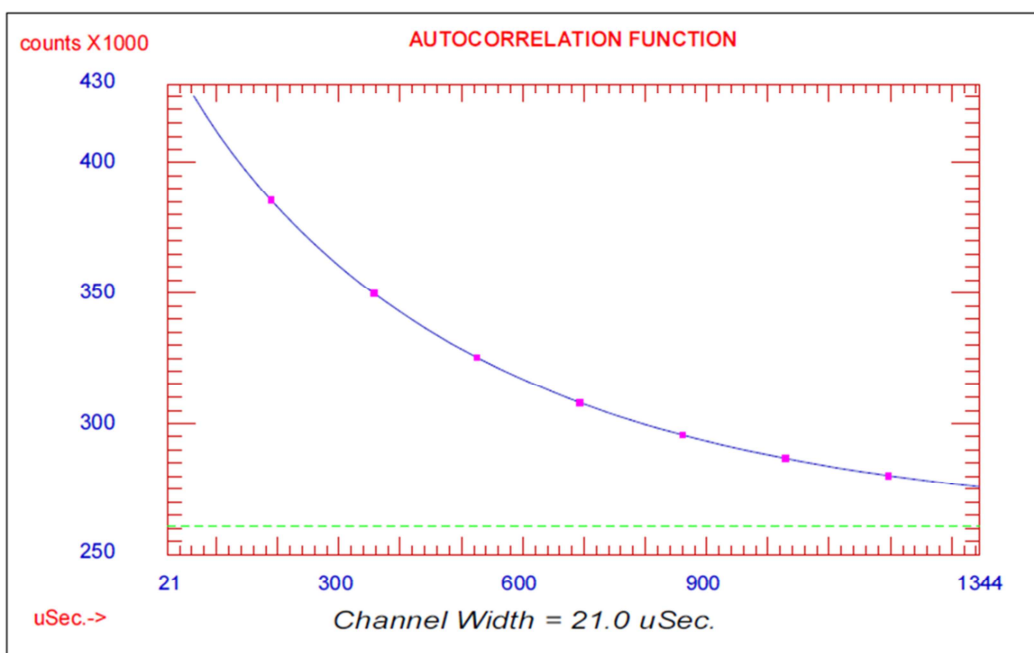


Figure S32. Autocorrelation function of the DLS measurement of poly(DMAAm)-*t*BuBnPE **4**.

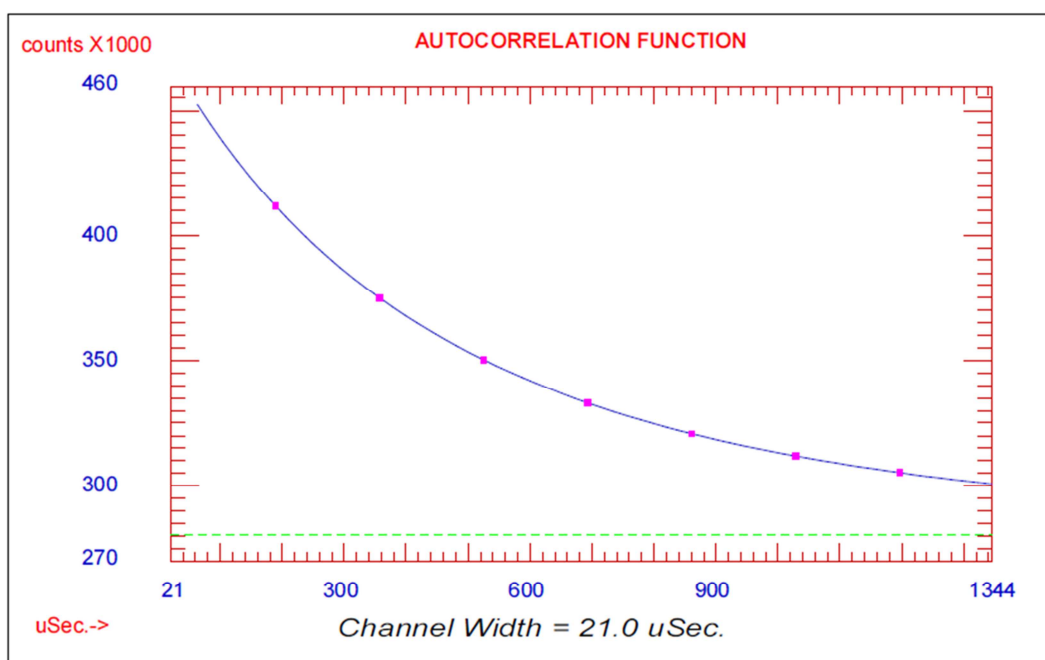


Figure S33. Autocorrelation function of the DLS measurement of the diblock copolymer **6**.

Formation of the supramolecular triblock copolymer (8a): The diblock copolymer **6** (30.00 mg, 0.003 mmol, 1.00 eq., 1.00 mmol L⁻¹, based on $M_n = 10000$ g mol⁻¹) was dissolved in 2.0 mL DMF. In a separate vial poly(NiPAAm)- β -CD **7a** (26.40 mg, 0.003 mmol, 1.00 eq.,

1.00 mmol L⁻¹, based on $M_n = 8800$ g mol⁻¹) was dissolved in DMF (1.0 mL) as well. The solution of **7** was slowly added to the solution of **6** and was stirred at ambient temperature for 30 min. Subsequently, the mixture was dialyzed against a gradient of deionized H₂O/DMF (70:30, 80:20, 90:10 and finally 100% H₂O) in a SpectraPor3 membrane (MWCO = 1000 Da). The inclusion complex of β -CD and the *tert*-butyl phenyl moiety was evidenced via 2D NOESY NMR in D₂O and DLS measurements in Milli-Q water with a concentration of 0.06 mmol L⁻¹ ($D_h \approx 23.0$ nm).

Table S8. Reaction conditions for supramolecular self-assembly of the β -CD-polymers with the covalently bound diblock copolymer **6**. The same reaction conditions apply as stated for the formation of poly(DEAAm)-*b*-poly(DMAAm)-*b*-poly(NiPAAm) **8a**.

| supramolecular block | M_n β -CD polymer [g mol ⁻¹] | c^0 Polymer [mmol L ⁻¹] | c^0 diblock copolymer 6 [mmol L ⁻¹] |
|----------------------|--|---------------------------------------|--|
| 8b | 10700 | 0.47 | 0.47 |
| 8c | 16400 | 1.00 | 1.00 |

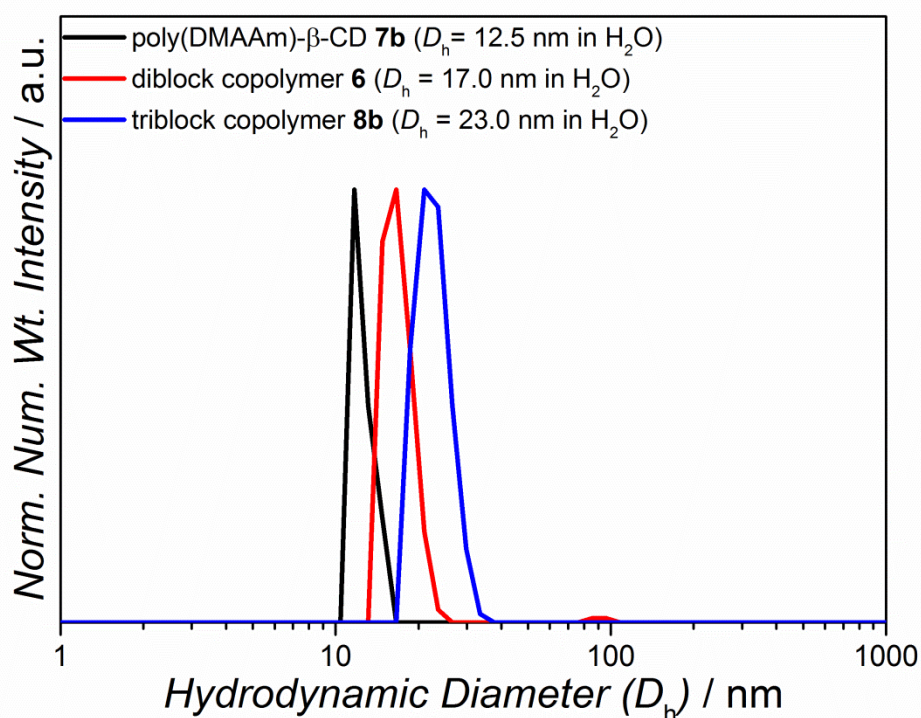


Figure S34. DLS measurements at 25 °C in Milli Q water, showing the number weighted size distributions of the β -CD functionalized polymer block poly(DMAAm)- β -CD **7b**, the diblock copolymer **6** and the supramolecularly formed triblock copolymer poly(DMAAm)-*b*-poly(DMAAm)-*b*-poly(DEAAm) **8b**. The samples were measured at a concentration of 0.06 mmol L⁻¹. The corresponding autocorrelation functions are listed below. The autocorrelation function for the diblock copolymer **6** is shown in **Figure S31**.

DLS autocorrelation functions:

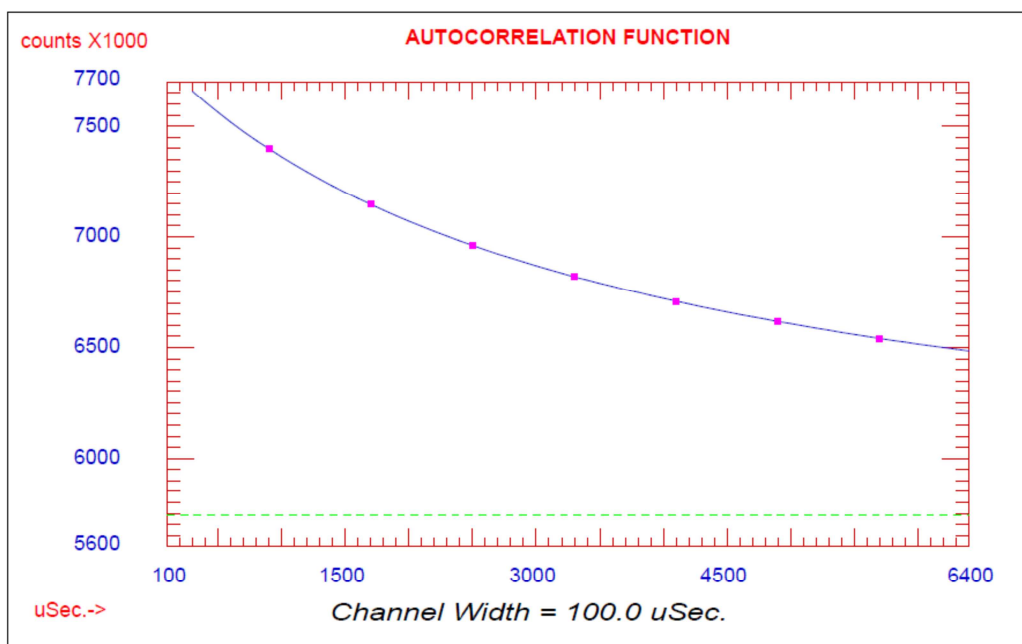


Figure S35. Autocorrelation function of the DLS measurement of poly(DMAAm)- β -CD 7.

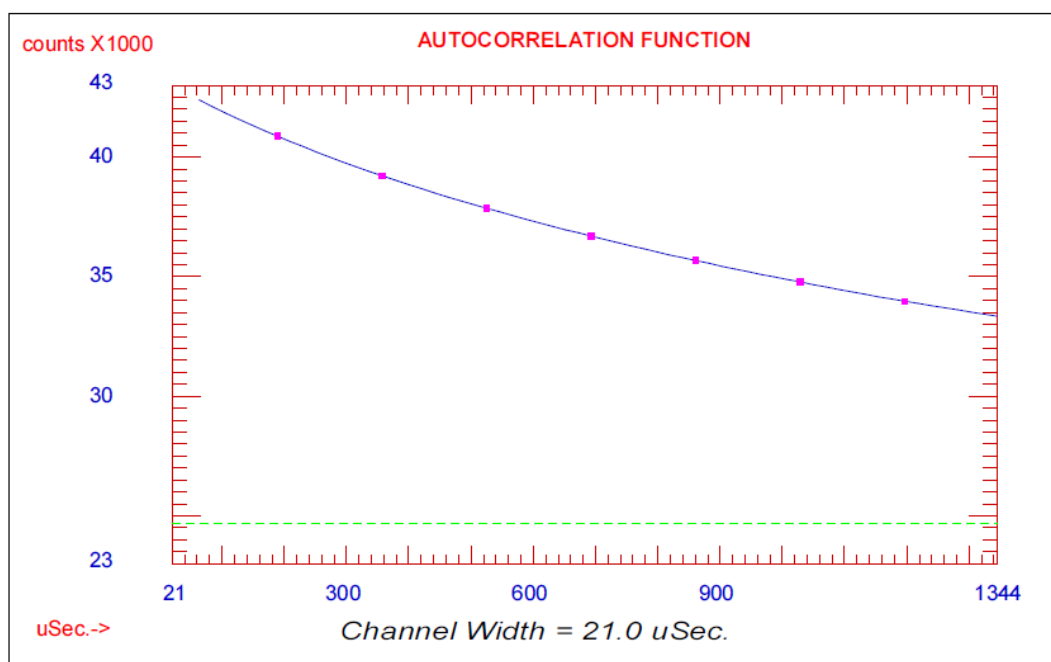


Figure S36. Autocorrelation function of the DLS measurement of the triblock copolymer poly(DMAAm)-*b*-poly(DMAAm)-*b*-poly(DEAAm) **8b**.

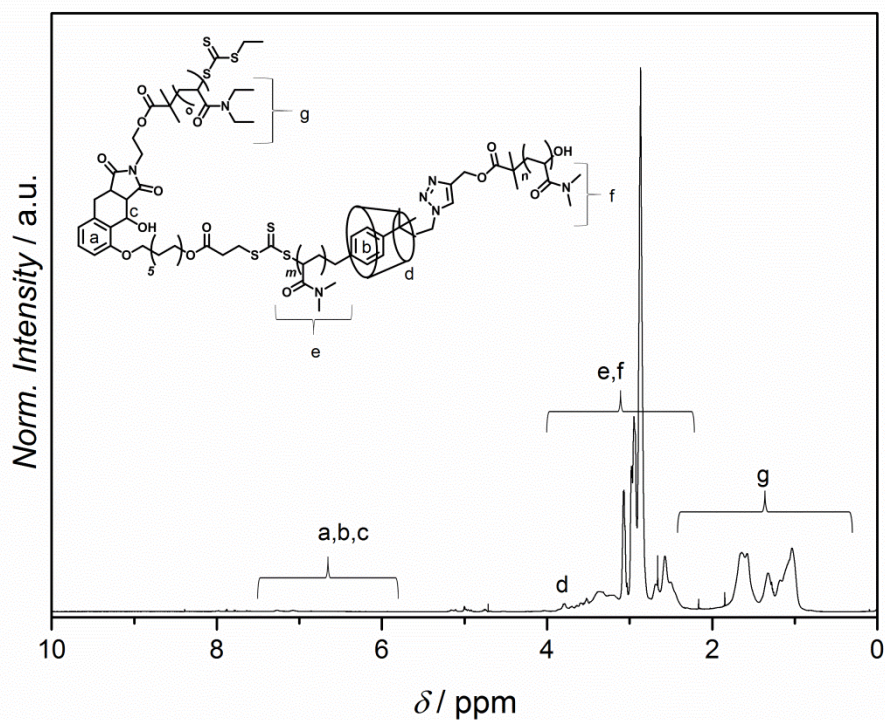


Figure S37. ^1H NMR spectrum (600 MHz, D_2O , 25 $^\circ\text{C}$) of the supramolecular diblock copolymer poly(DMAAm)-*b*-poly(DMAAm)-*b*-poly(DEAAm) **8b**. For overview reasons only the specific peaks of the polymer and the linking points are assigned.

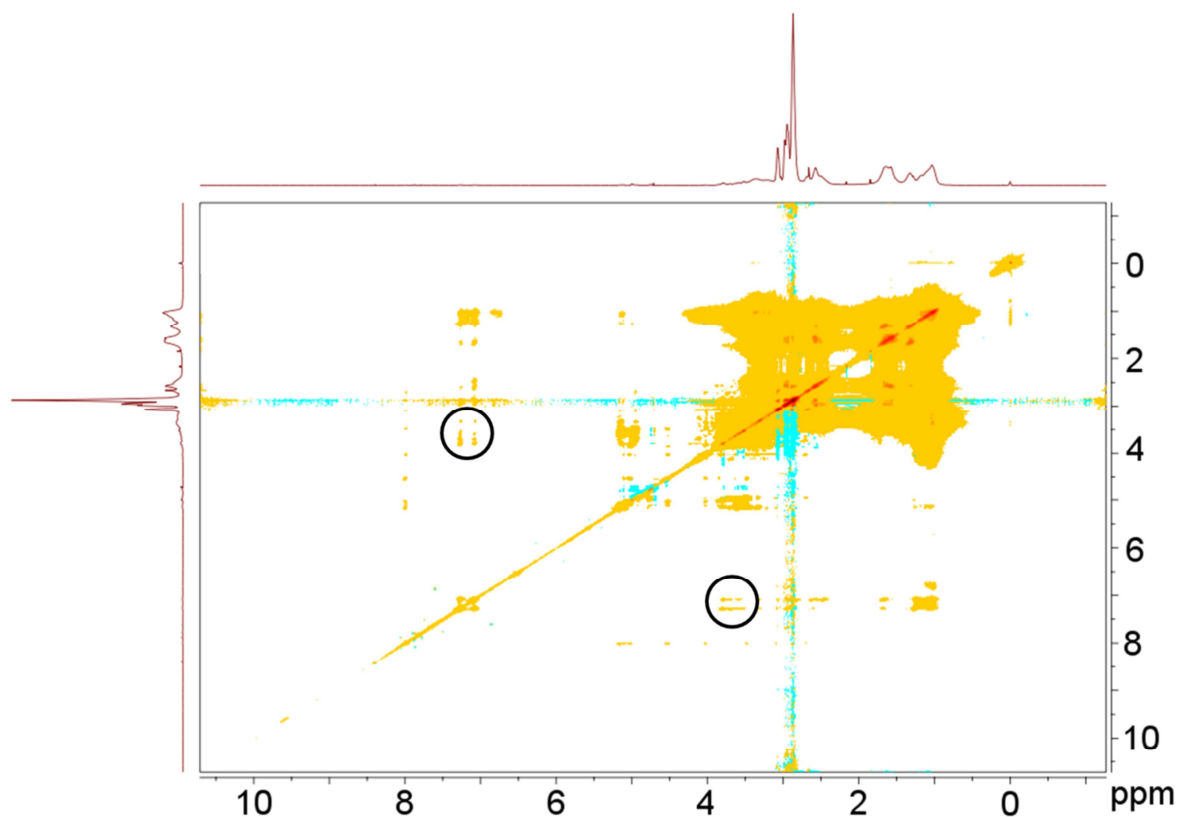


Figure S38. 2D NOESY NMR spectrum of the supramolecular triblock copolymer poly(DMAAm)-*b*-poly(DMAAm)-*b*-poly(DEAAm) **8b** in D_2O at 25 $^\circ\text{C}$. The cross-correlation peaks evidencing the close proximity of the inner protons of $\beta\text{-CD}$ (3.6 ppm and 3.8 ppm) and the *tert*-butyl benzyl protons (7.10 ppm and 7.30 ppm) are circled in the spectrum.

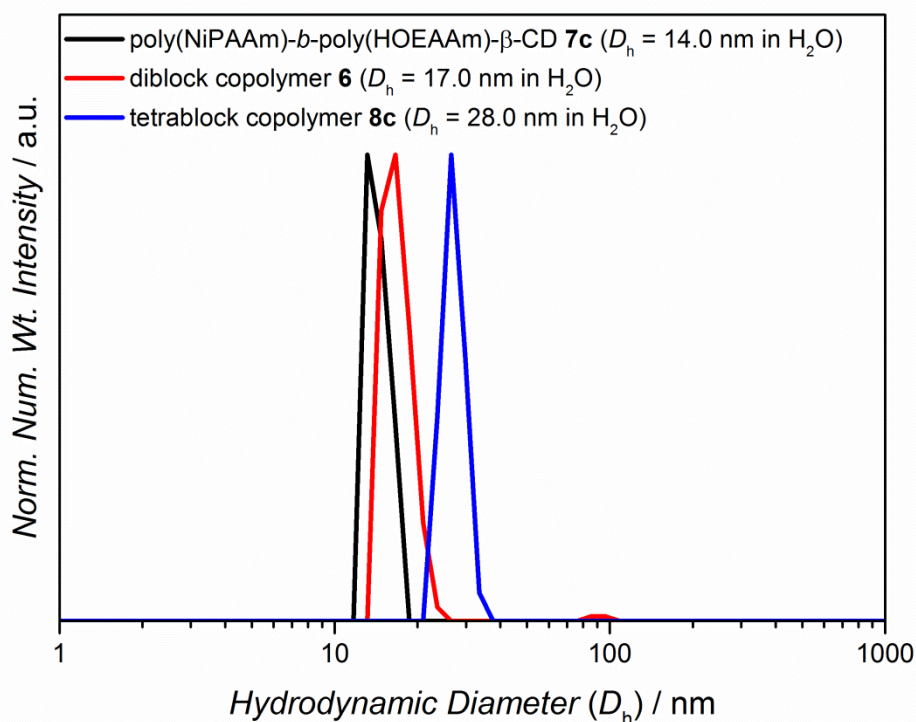


Figure S39. DLS measurements at 25 °C in Milli Q water, showing the number weighted size distributions of the β -CD functionalized diblock copolymer poly(NiPAAm)-*b*-poly(HOEAAM)- β -CD **7c**, the diblock copolymer **6** and the supramolecularly formed tetrablock copolymer poly(NiPAAm)-*b*-poly(HOEAAM)-*b*-poly(DMAAm)-*b*-poly(DEAAm) **8c**. The samples were measured at a concentration of 0.06 mmol L⁻¹. The corresponding autocorrelation functions are listed below. The autocorrelation function for the diblock copolymer **6** is shown in Figure S31.

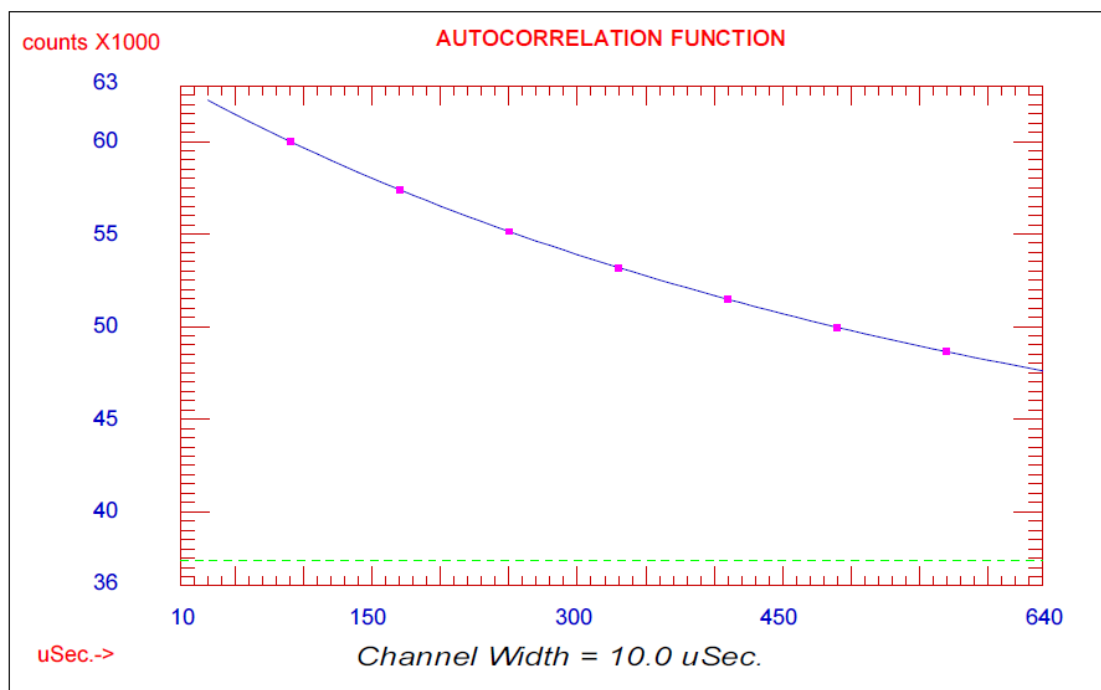


Figure S40. Autocorrelation function of the DLS measurement of poly(NiPAAm)-*b*-poly(HOEAAM)- β -CD **7c**.

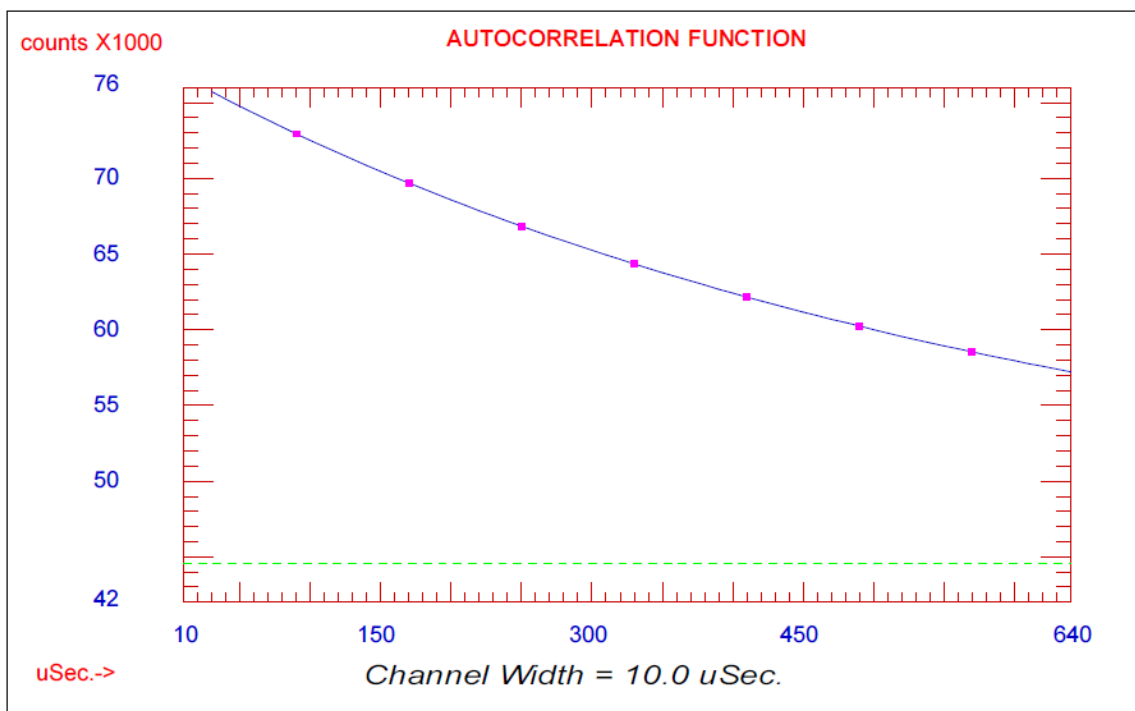


Figure S41. Autocorrelation function of the DLS measurement of the tetrablock copolymer poly(NiPAAm)-*b*-poly(HOEAAm)-*b*-poly(DMAAm)-*b*-poly(DEAAm) **8c**.

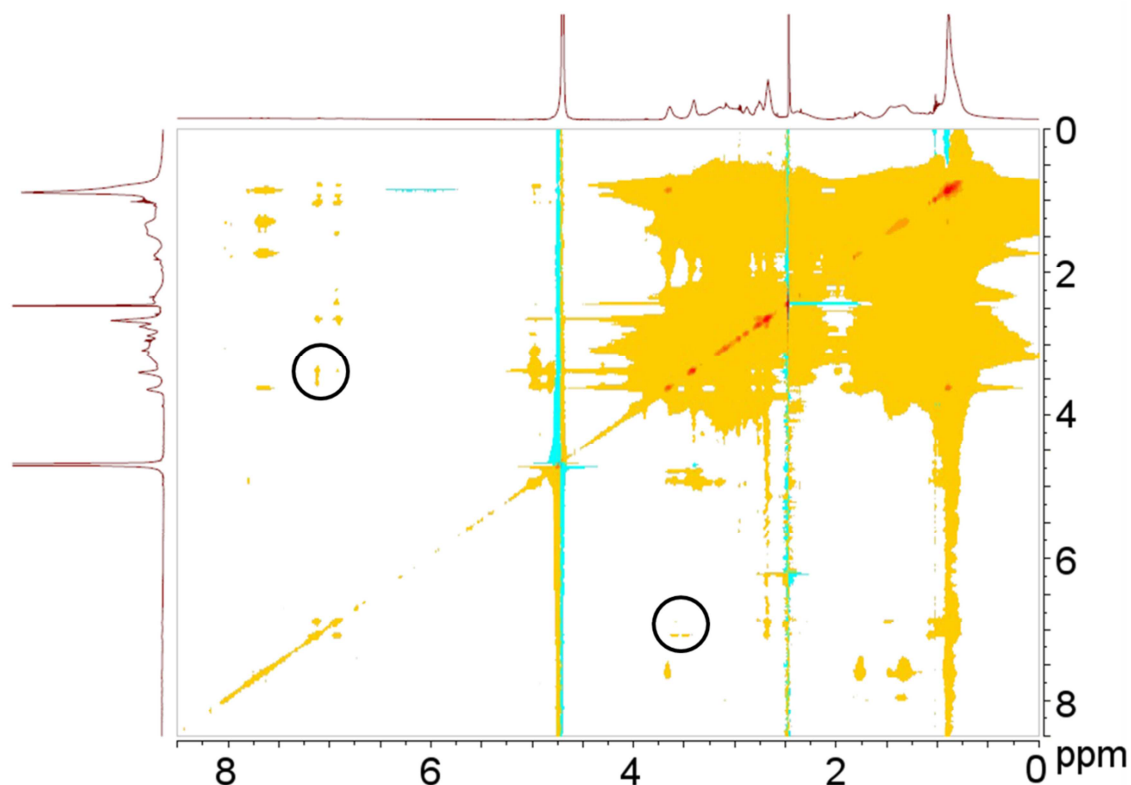


Figure S42. 2D NOESY NMR spectrum of the supramolecular tetrablock copolymer poly(NiPAAm)-*b*-poly(HOEAAm)-*b*-poly(DMAAm)-*b*-poly(DEAAm) **8c** in D₂O at 25 °C. The cross-correlation peaks evidencing the close proximity of the inner protons of β -CD (3.10 ppm, 3.37 ppm and 3.57 ppm) and the *tert*-butyl benzyl protons (6.90 ppm and 7.10 ppm) are circled in the spectrum.

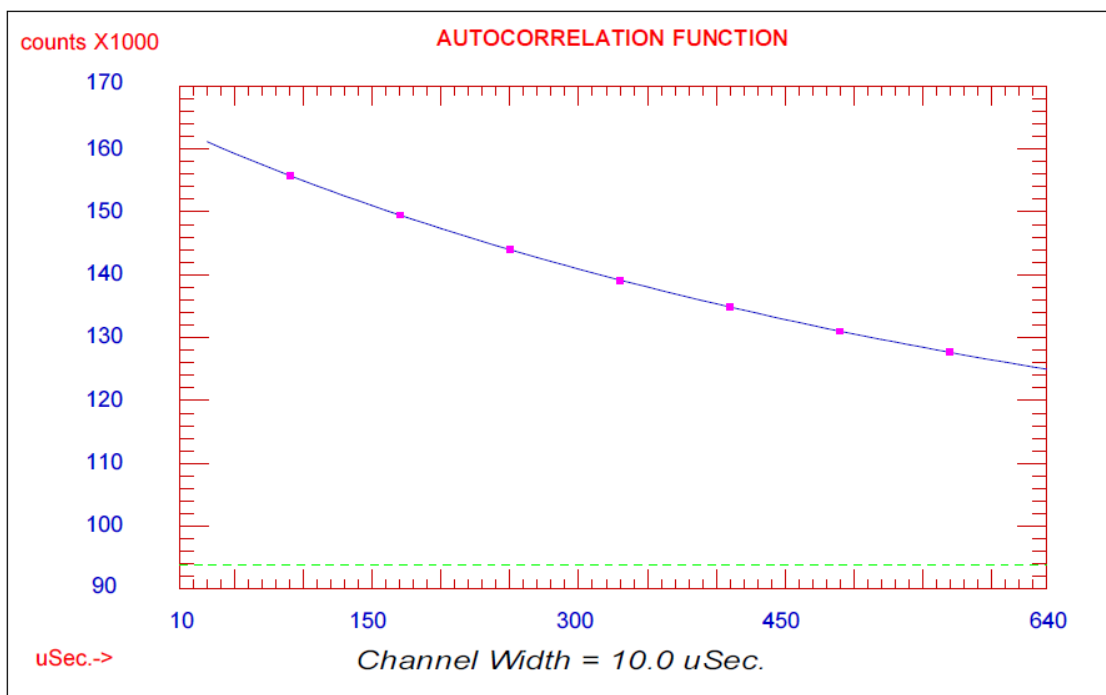


Figure S43. Autocorrelation function of the DLS measurement of poly(NiPAAm)- β -CD **8a**.

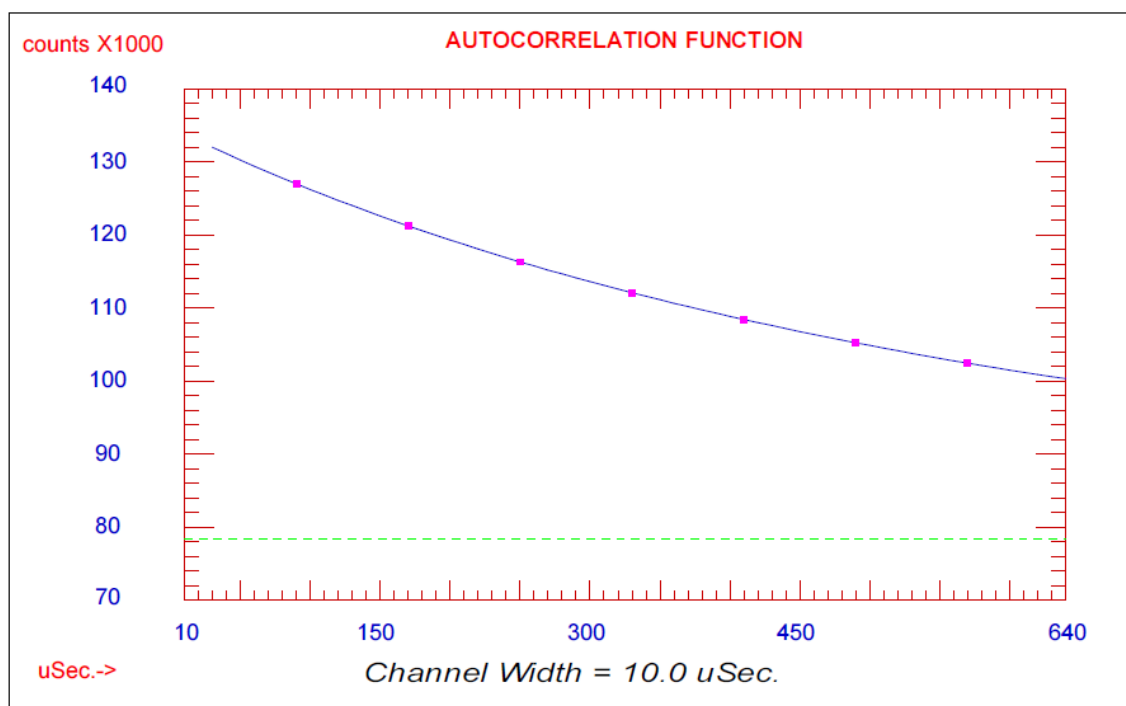


Figure S44. Autocorrelation function of the DLS measurement of the triblock copolymer poly(NiPAAm)-*b*-poly(DMAAm)-*b*-poly(DEAAm) **8a**.

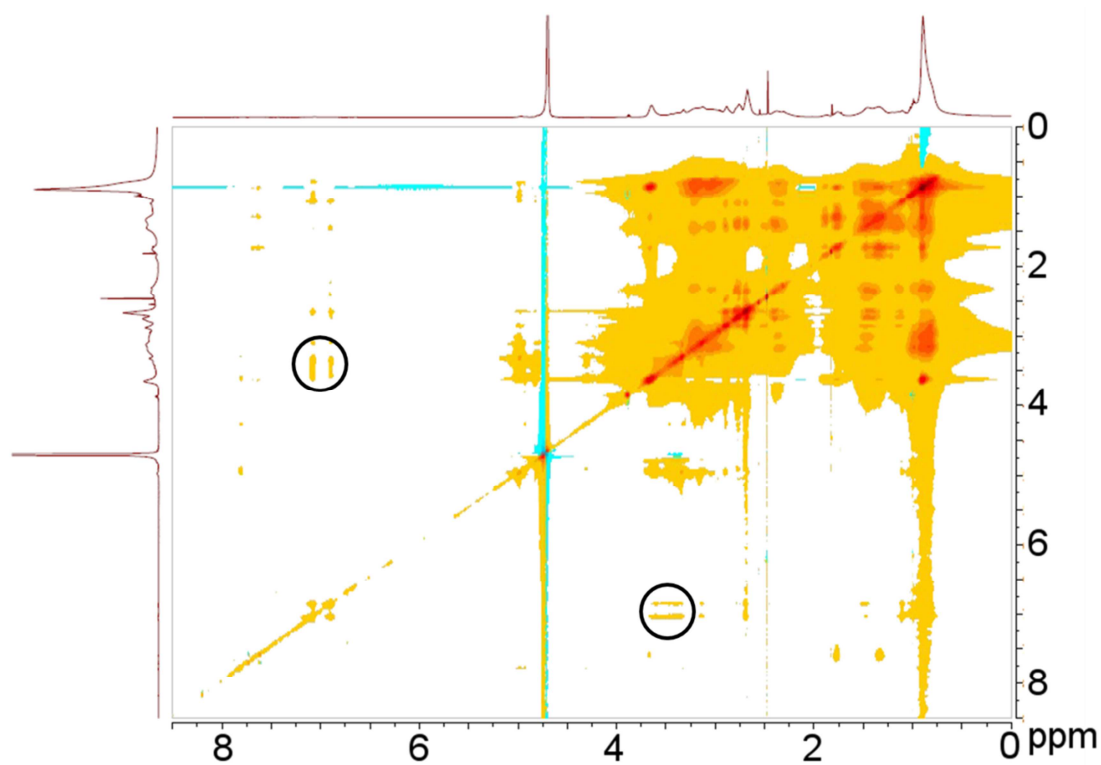


Figure S45. 2D NOESY NMR spectrum of the supramolecular triblock copolymer poly(NiPAAm)-*b*-poly(DMAAm)-*b*-poly(DEAAm) **8a** in D₂O at 25 °C. The cross-correlation peaks evidencing the close proximity of the inner protons of β-CD (3.10 ppm, 3.37 ppm and 3.57 ppm) and the *tert*-butyl benzyl protons (6.90 ppm and 7.10 ppm) are circled in the spectrum.

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