Supporting Information for

Supramolecular Polymer Networks of Building Blocks Prepared via RAFT Polymerization

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Additional Experimental Procedures

*Synthesis of bis(6-(adamantan-1-ylamino)-6-oxohexyl) 2,2'-(thiocarbonylbis(sulfanediyl))-bis(2-methylpropanoate) (**CTA1**)*

CMP (0.25 g, 0.88 mmol, 1.0 eq.), *N*-(adamantan-1-yl)-6-hydroxyhexanamide (0.75 g, 2.83 mmol, 3.2 eq.) and triphenylphosphine (0.74 g, 2.82 mmol, 3.2 eq.) were dissolved in dry THF (10 mL) in a 50 mL round bottom flask. At 0 °C, DIAD (0.6 mL, 3.06 mmol, 3.5 eq.) in dry THF (5 mL) was added dropwise. The reaction mixture was stirred at ambient temperature overnight and additionally stirred for 3 h at 40 °C. After cooling to ambient temperature, DCM (30 mL) was added and the organic phase was washed with saturated $NaHCO_3$-solution (2×30 mL). The organic phase was dried over magnesium sulfate, filtered and concentrated in vacuo. The residue was purified via column chromatography on silica-gel with *n*-hexane/ethyl acetate as eluent that was gradually changed from 3:1 to 1:1. The purified product was obtained as yellow oil (0.52 g, 0.67 mmol, 76%).

^{1}H-NMR (400 MHz, $CDCl_3$): [δ, ppm] = 5.32 (br s, 2H, N***H***), 4.05 (t, 4H, C***H***$_2$-O-C=O), 2.12 - 2.02 (m, 10 H, 6x ***C***H$_{adamantyl}$; 2x C***H***$_2$-C=O), 2.01 - 1.94 (m, 12H, 6x C***H***$_{2,adamantyl}$-C-NH), 1.73 - 1.51 (m, 28H, 4x (C***H***$_3$)$_2$-C; 2x C***H***$_2$-CH$_2$-C=O; 6x C***H***$_{2,adamantyl}$), 1.40 - 1.29 (m, 4H, 2x C***H***$_2$-CH$_2$-O), 1.28 - 1.18 (m, 4H, 2x C***H***$_2$-CH$_2$-CH$_2$-C=O).

^{13}C-NMR (100 MHz, $CDCl_3$): [δ, ppm] = 218.6 (***C***=S), 172.2 and 172.9 (4x ***C***=O), 66.1 (2x ***C***H$_2$-O-C=O), 56.3 (2x ***C***(CH$_3$)$_2$), 51.9 (2x ***C***-NH), 41.8 (6x ***C***H$_{2,adamantyl}$-C-NH), 37.6 (2x ***C***H$_2$-C=O), 36.5 (6x ***C***H$_{2,adamantyl}$), 29.6 (6x ***C***H$_{adamantyl}$), 28.3 (2x ***C***H$_2$-CH$_2$-O-C=O), 25.7 and 25.5 (2x ***C***H$_2$-CH$_2$-CH$_2$-C=O; 2x ***C***H$_2$-CH$_2$-C=O), 25.3 (4x (***C***H$_3$)$_2$-C).

ESI-MS: $[M + Na^+]_{exp}$ = 799.33 *m*/*z* and $[M + Na^+]_{calc}$ = 799.38 *m*/*z* (refer to Figure S5).

Synthesis of N,N,N-(tris-1-(mono-(6-desoxy)-β-CD)-1H-1,2,3-triazol-4-yl)methanamine (β-CD_3)

Modified from a literature procedure,[1,2] in a 50 mL Schlenk tube equipped with a stirring-bar tripropargylamine (34 mg, 0.26 mmol, 1.0 eq.), β-CD-N_3 (1.00 g, 0.86 mmol, 3.3 eq.) and PMDETA (0.16 mL, 0.77 mmol, 3.0 eq.) were dissolved in DMF (11 mL). The reaction mixture was degassed by three freeze-pump-thaw cycles and the tube was backfilled with argon before CuBr (112 mg, 0.78 mmol, 3.0 eq.) was added under a flow of argon. The tube was sealed again and subjected to two additional freeze-pump-thaw cycles. After the tube was backfilled with argon, the reaction vessel was immersed in an oil bath at 70 °C for 4 d. After cooling to ambient temperature the product was precipitated in an excess of acetone. The product was filtered, dissolved in 5 wt.% EDTA-solution (10 mL) and dialyzed with a SpectraPor3 membrane (MWCO = 2000 Da) for 3 days at ambient temperature. The solvent was removed by lyophilization to yield β-CD_3 as an off-white solid (574 mg, 0.16 mmol, 61%).

^{1}H NMR (600 MHz, D_2O): [δ, ppm] = 8.04 (s, 3H, 3x $\boldsymbol{H}_{triazole}$), 5.15 - 4.98 (m, 21H, 18x CD-C***H***-1; 3x CD-C***H***-1'), 4.69 (dd, 3H, 3x N-C***H****(gem)*$_2$-triazole), 4.27 (t, 3H, 3x N-C***H****(gem)*$_2$-triazole), 4.11 - 3.44 (m, 120H, 21x CD-C***H***-2,3,4,5; 18x CD-C***H***$_2$-6), 3.21 (d, 3H, 3x CD-C***H****(gem)*$_2$-6'), 2.95 (d, 3H, 3x CD-C***H****(gem)*$_2$-6').

ESI-MS: $[M + 2Na^{2+}]_{exp}$ = 1828.33 *m*/*z* and $[M + 2Na^{2+}]_{calc}$ = 1828.0926 *m*/*z* (refer to Figure S6 and Table S2).

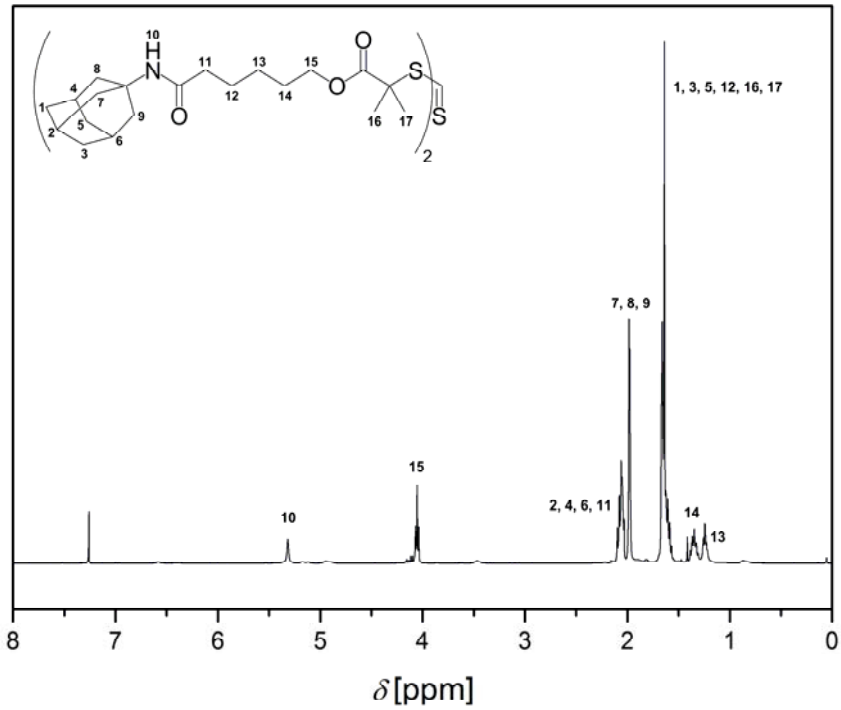

Figure S1. ^{1}H-NMR spectrum of bis(6-(adamantan-1-ylamino)-6-oxohexyl) 2,2'-(thiocarbonylbis(sulfanediyl))bis(2-methylpropanoate) (**CTA1**) in $CDCl_3$.

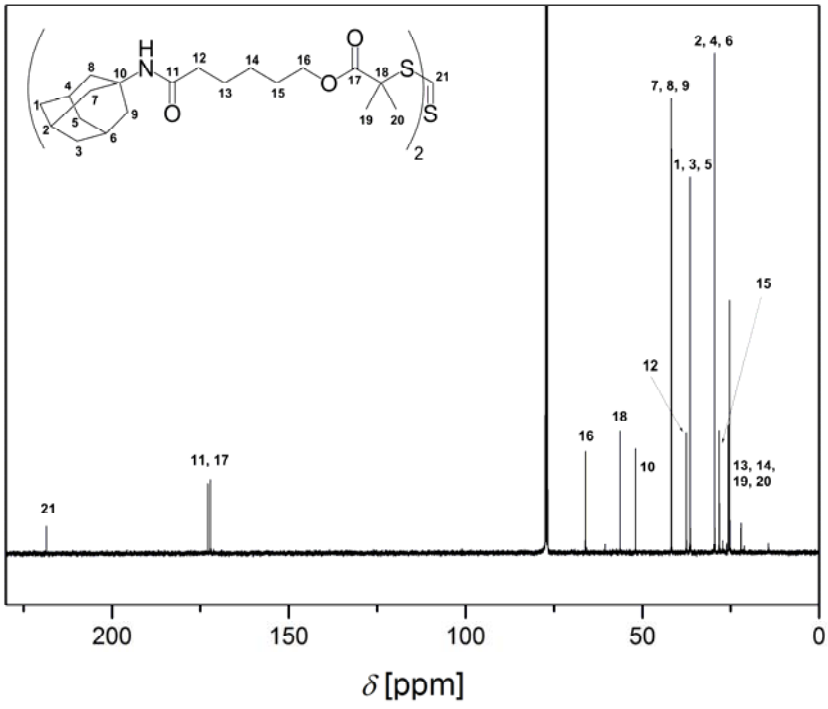

Figure S2. ^{13}C-NMR spectrum of bis(6-(adamantan-1-ylamino)-6-oxohexyl) 2,2'-(thiocarbonylbis(sulfanediyl))bis(2-methylpropanoate) (**CTA1**) in $CDCl_3$.

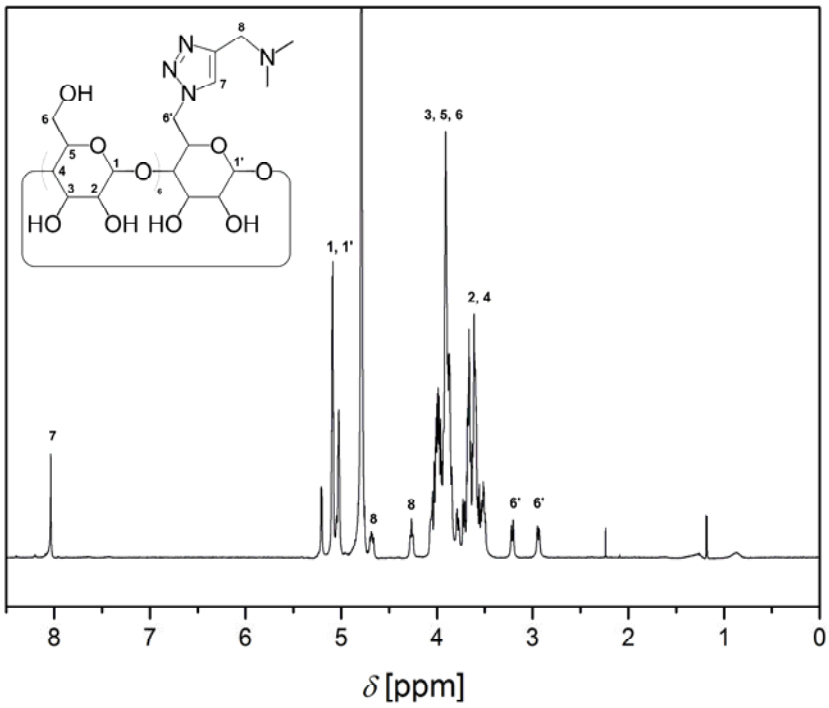

Figure S3. ^{1}H-NMR spectrum of *N*,*N*,*N*-(tris-1-(mono-(6-desoxy)-β-CD)-1H-1,2,3-triazol-4-yl)methanamine (β-CD_3) in D_2O.

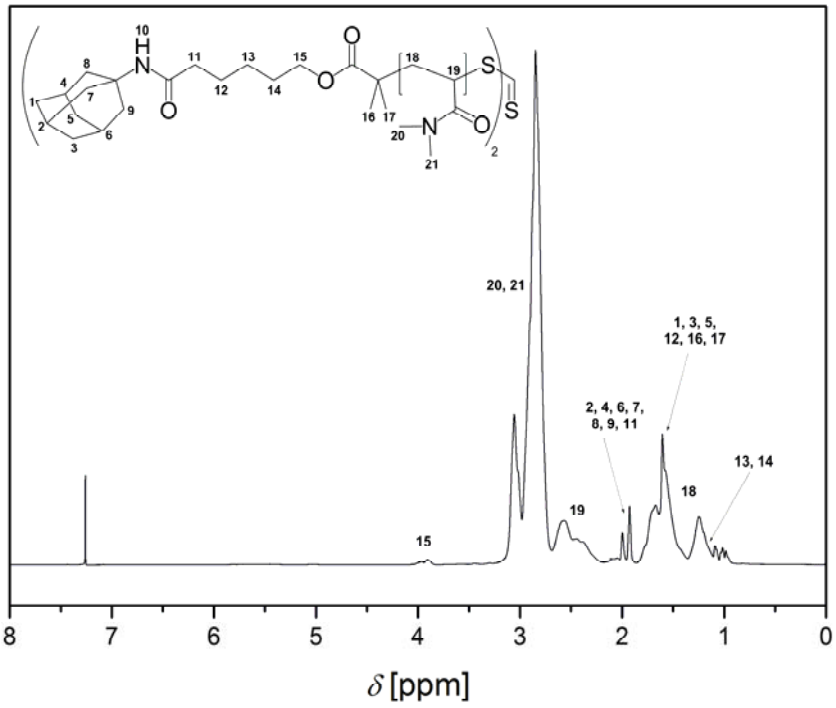

Figure S4. ^{1}H-NMR spectrum of $PDMA_{122}$-ADA_2 in $CDCl_3$.

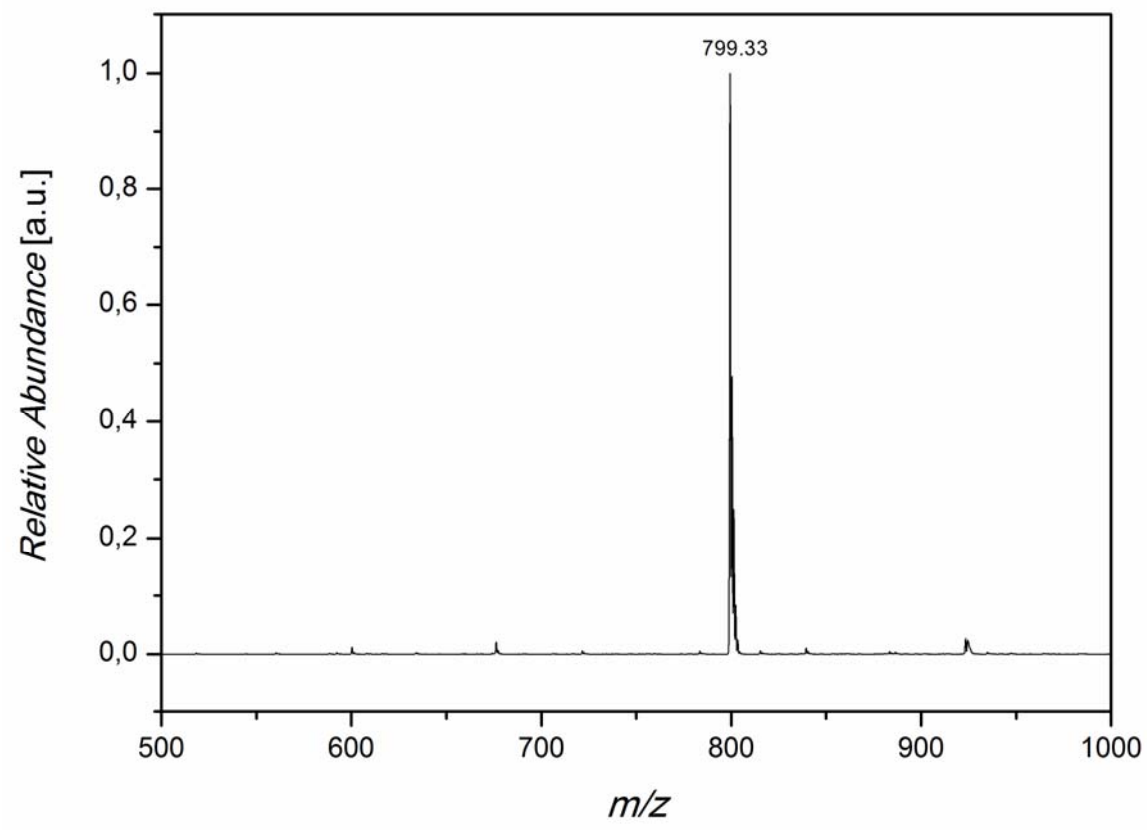

Figure S5. ESI-MS-spectrum of **CTA1** (ionized with NaI)

Table S1. Theoretical and experimental *m/z* of **CTA1** (ionized with NaI).

Species	m/z_{theo}	m/z_{exp}	$\Delta m/z$
$[CTA1 + Na^+]^+$	799.38	799.33	0.05

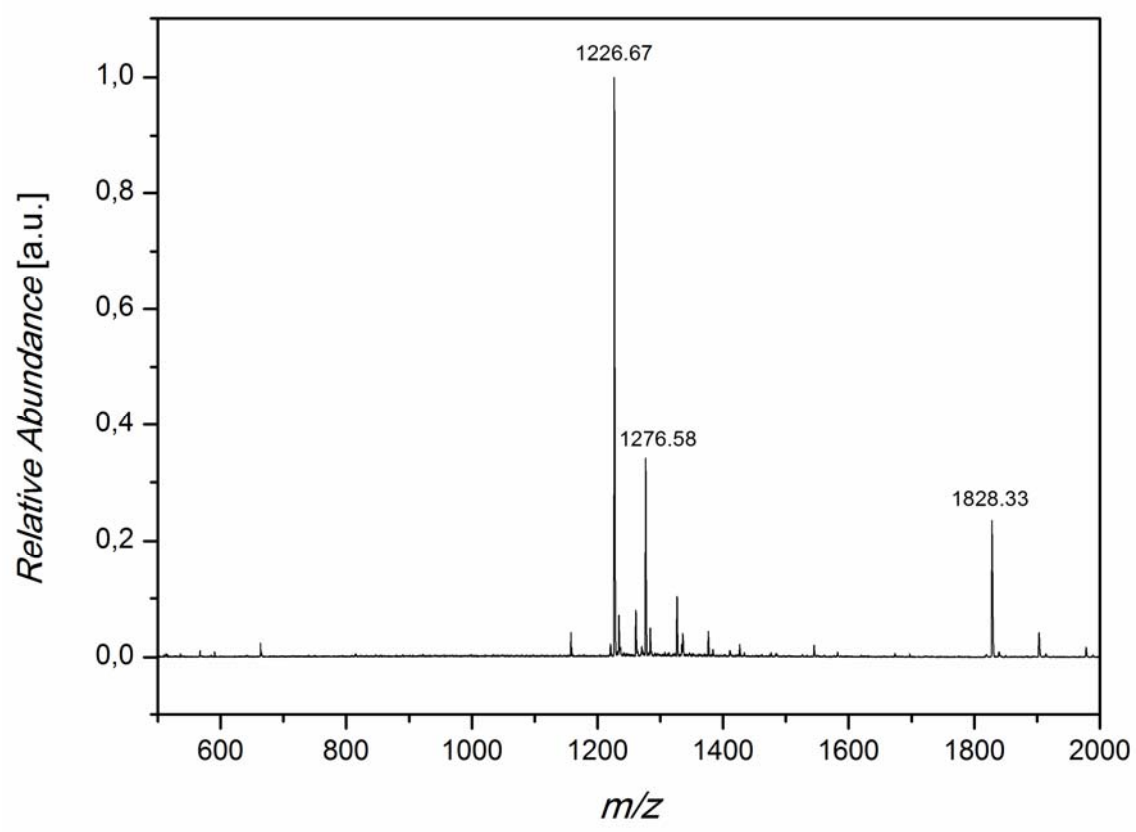

Figure S6. ESI-MS-spectrum of β-CD_3 (ionized with NaI).

Table S2. Theoretical and experimental *m/z* of β-CD_3 (ionized with NaI).

Species	m/z_{theo}	m/z_{exp}	$\Delta m/z$
$[\beta\text{-}CD_3 + 2Na^+]^{2+}$	1828.09	1828.33	0.24
$[\beta\text{-}CD_3 + 4Na^+ + I^-]^{3+}$	1276.66	1276.58	0.22
$[\beta\text{-}CD_3 + 3Na^+]^{3+}$	1226.39	1226.67	0.28

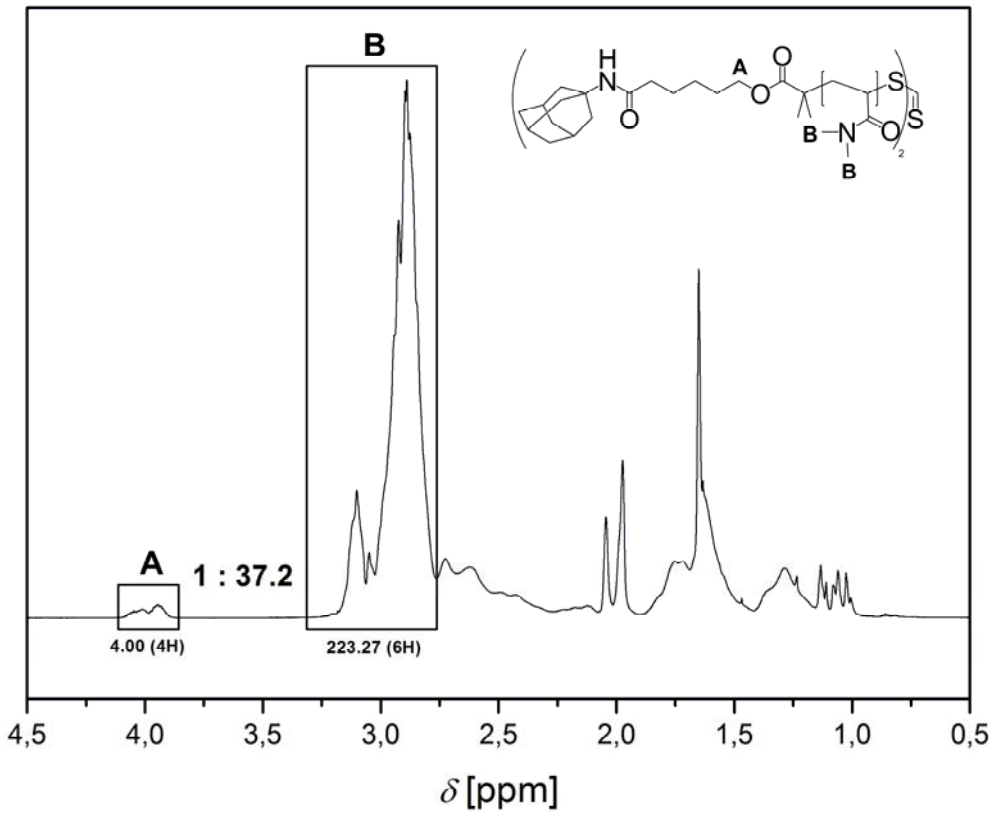

Figure S7. Exemplary calculation of the polymerization degree of $PDMA_{37}$-ADA_2.

Table S3. Calculated polymerization degrees ($P_{n,NMR}$) and molecular weights ($M_{n.NMR}$) of $PDMA_X$-ADA_2 based on NMR data.

Polymer	$P_{n,NMR}$	$M_{n,NMR}$ [g mol^{-1}]
$PDMA_{37}$-ADA_2	37.2	4500
$PDMA_{122}$-ADA_2	122.4	12900
$PDMA_{213}$-ADA_2	212.6	21900
$PDMA_{307}$-ADA_2	306.9	31200
$PDMA_{422}$-ADA_2	422,2	42600

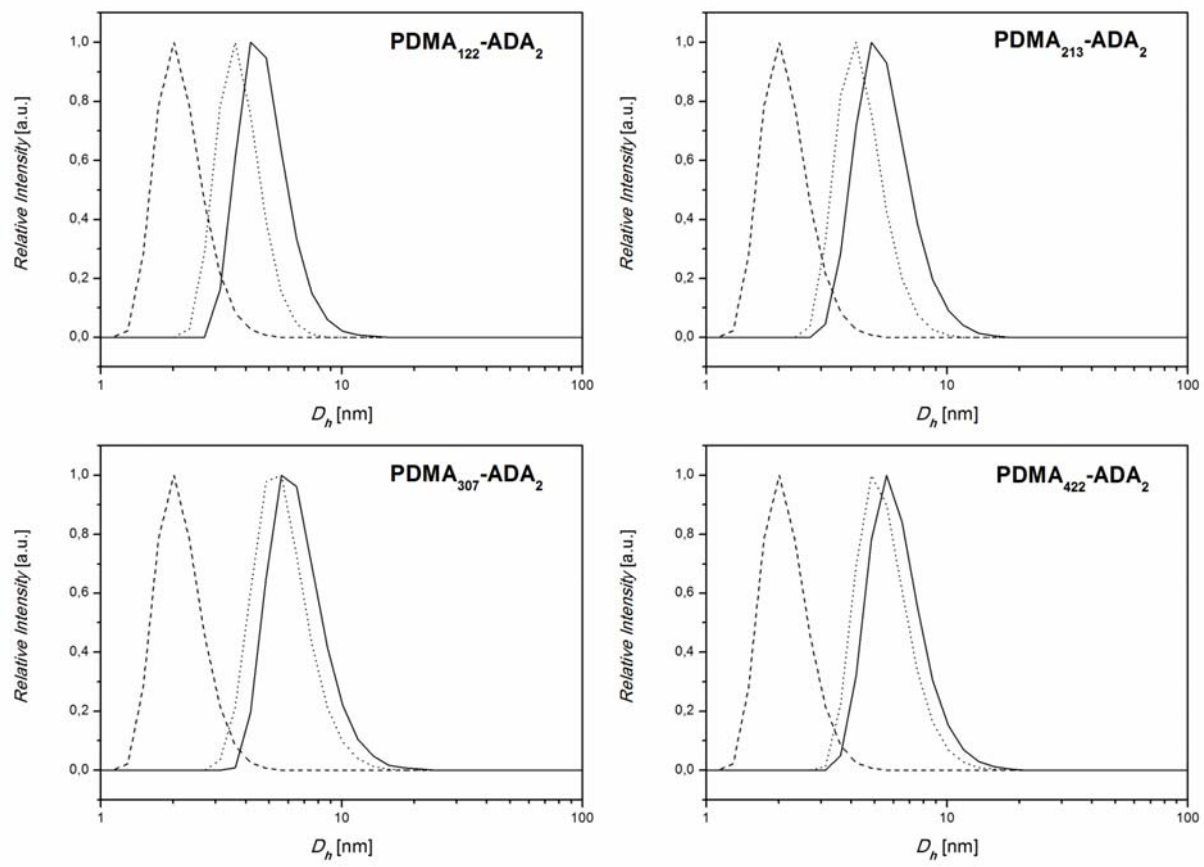

Figure S8. Number-weighted size distributions for the β-CD_3 trilinker (dashed line), $PDMA_X$-ADA_2 (dotted line), and the supramolecular complexes with an ADA/CD ratio of 1:1 (solid line) in water at 25 °C.

Table S4. Viscosity values in Pas derived from steady shear measurements of $PDMA_X$-ADA_2 and β-CD_3 solutions depending on concentration at 20 °C.

Polymer	5 mM	10 mM	15 mM	20 mM
β-CD_3	0.0035	0.0035	0.0035	0.0034
$PDMA_{37}$-ADA_2	0.0035	0.0040	0.0043	0.0046
$PDMA_{122}$-ADA_2	0.0045	0.0075	0.0113	0.0146
$PDMA_{213}$-ADA_2	0.0051	0.0256	0.0435	0.0680
$PDMA_{307}$-ADA_2	0.0200	0.0907	0.2939	0.6976
$PDMA_{422}$-ADA_2	0.0325	0.1843	0.6847	2.3670

Table S5. Viscosity values in Pas derived from steady shear measurements of $PDMA_X$-ADA_2/β-CD_3 mixtures with a CD/ADA ratio of 1:2 depending on concentration at 20 °C.

Polymer	5 mM	10 mM	15 mM	20 mM
$PDMA_{37}$-ADA_2	0.0040	0.0053	0.0068	0.0081
$PDMA_{122}$-ADA_2	0.0063	0.0125	0.0183	0.0263
$PDMA_{213}$-ADA_2	0.0126	0.0404	0.0889	0.1468
$PDMA_{307}$-ADA_2	0.0418	0.2116	0.8120	1.5850
$PDMA_{422}$-ADA_2	0.0694	0.4917	2.2080	4.0730

Table S6. Viscosity values in Pas derived from steady shear measurements of $PDMA_X$-ADA_2/β-CD_3 mixtures with a CD/ADA ratio of 2:2 depending on concentration at 20 °C.

Polymer	5 mM	10 mM	15 mM	20 mM
$PDMA_{37}$-ADA_2	0.0048	0.0126	0.0327	0.0478
$PDMA_{122}$-ADA_2	0.0073	0.0165	0.0365	0.0561
$PDMA_{213}$-ADA_2	0.0281	0.1091	0.2190	0.3579
$PDMA_{307}$-ADA_2	0.0693	0.4432	1.1490	2.4330
$PDMA_{422}$-ADA_2	0.0967	0.5820	2.8440	5.9600

Table S7. Viscosity values in Pas derived from steady shear measurements of $PDMA_X$-ADA_2/β-CD_3 mixtures with a CD/ADA ratio of 3:2 depending on concentration at 20 °C.

Polymer	5 mM	10 mM	15 mM	20 mM
$PDMA_{37}$-ADA_2	0.0058	0.0168	0.0423	0.0930
$PDMA_{122}$-ADA_2	0.0082	0.0247	0.0596	0.1346
$PDMA_{213}$-ADA_2	0.0379	0.1288	0.5327	0.8634
$PDMA_{307}$-ADA_2	0.1127	0.7722	3.4310	6.1830
$PDMA_{422}$-ADA_2	0.1850	1.6470	8.5040	11.7400

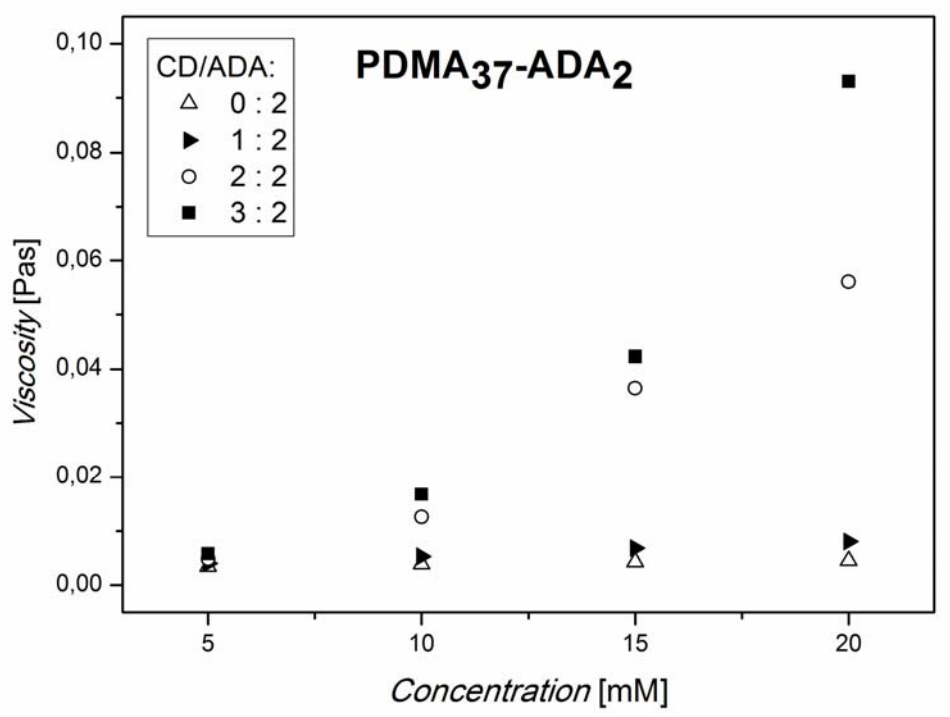

Figure S9. Viscosity values in Pas for $PDMA_{37}$-ADA_2 and different CD/ADA ratios depending on the polymer concentration at 20 °C.

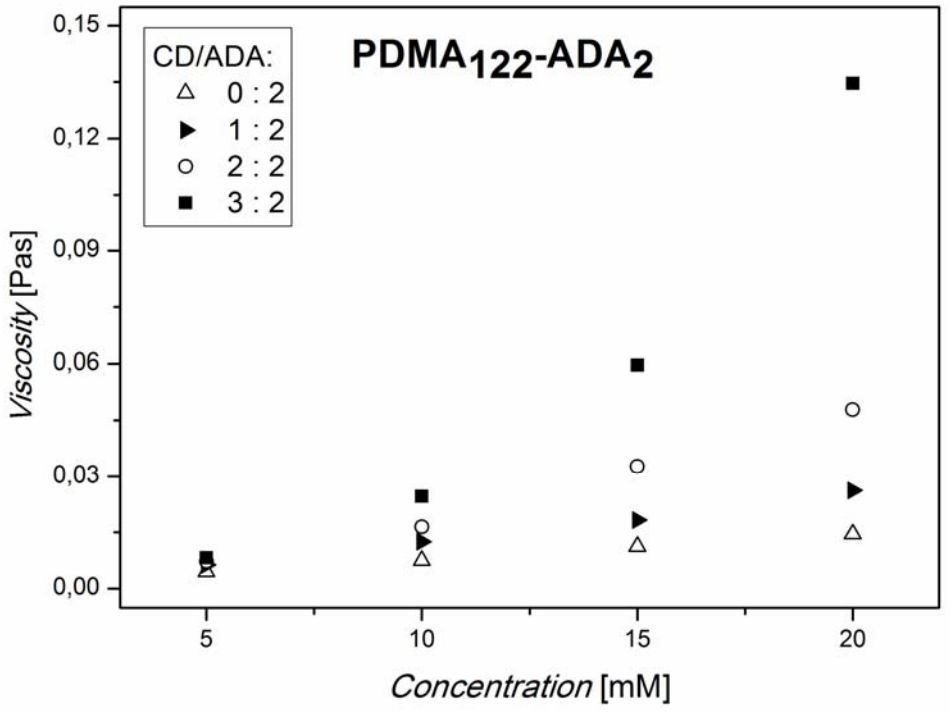

Figure S10. Viscosity values in Pas for $PDMA_{122}$-ADA_2 and different CD/ADA ratios depending on the polymer concentration at 20 °C.

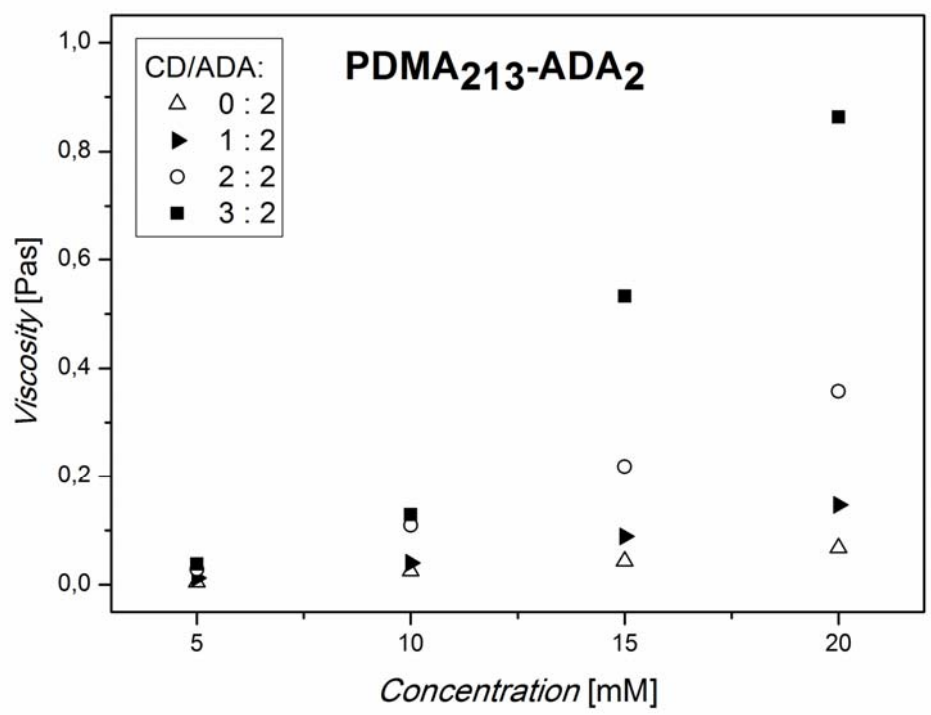

Figure S11. Viscosity values in Pas for $PDMA_{213}$-ADA_2 and different CD/ADA ratios depending on the polymer concentration at 20 °C.

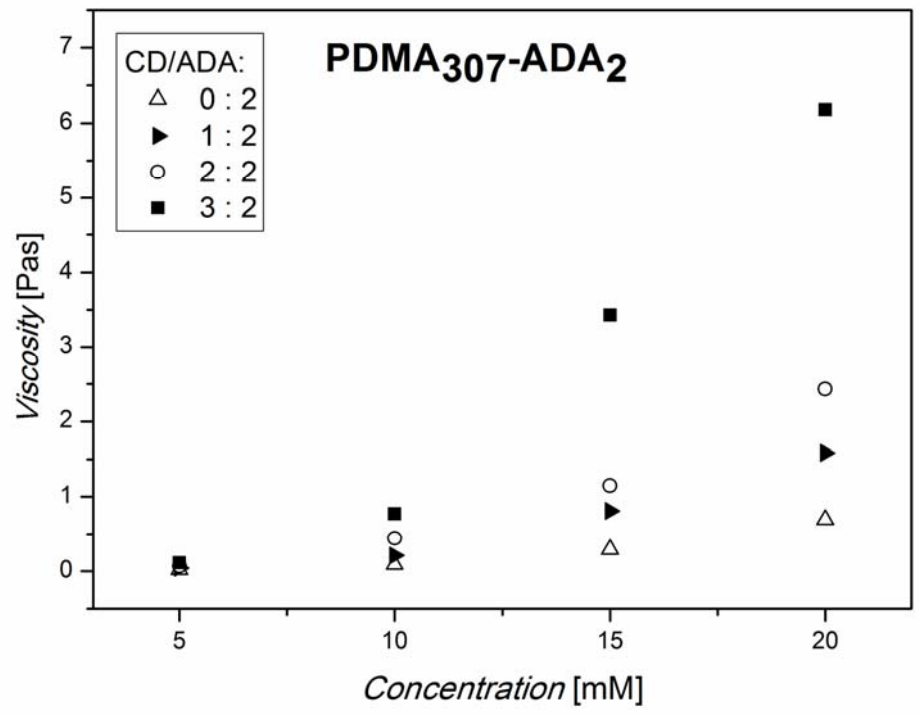

Figure S12. Viscosity values in Pas for $PDMA_{307}$-ADA_2 and different CD/ADA ratios depending on the polymer concentration at 20 °C.

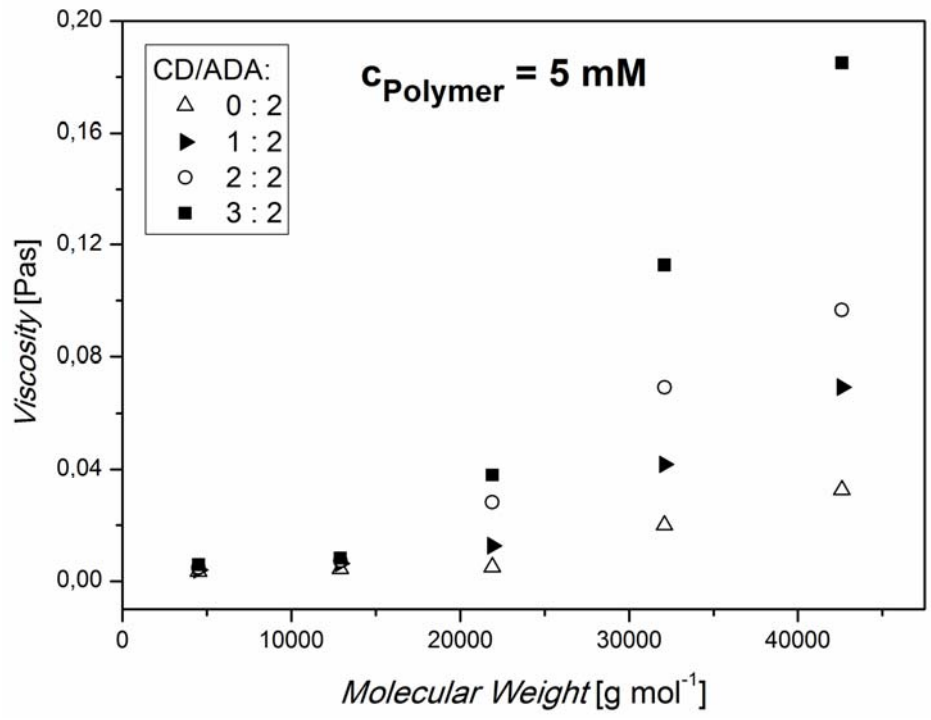

Figure S13. Viscosity values in Pas for $c_{Polymer}$ = 5 mM and different CD/ADA ratios depending on the molecular weight of $PDMA_X$-ADA_2 at 20 °C.

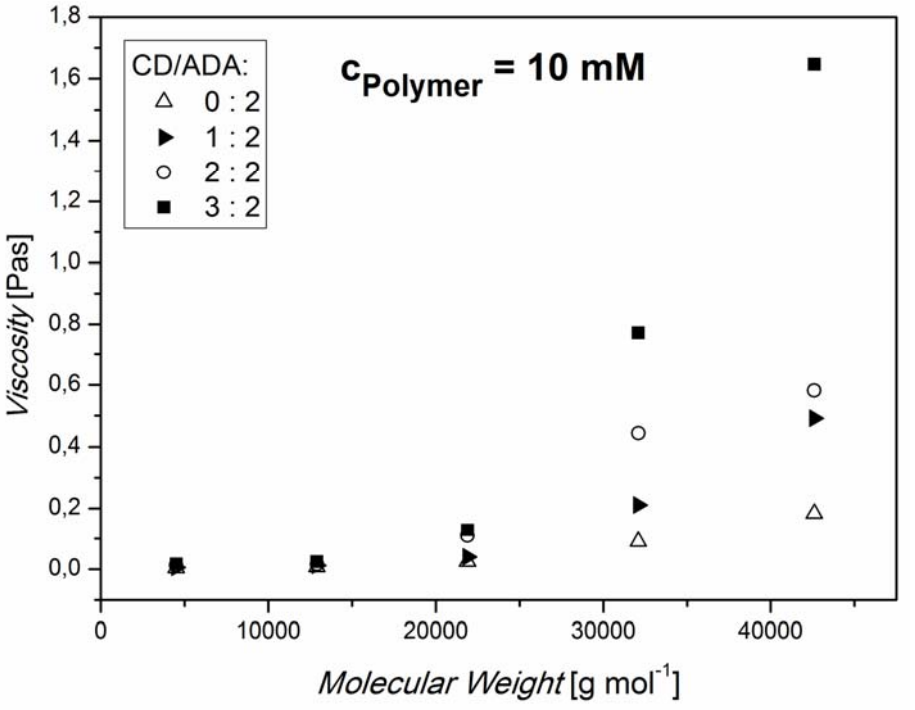

Figure S14. Viscosity values in Pas for $c_{Polymer}$ = 10 mM and different CD/ADA ratios depending on the molecular weight of $PDMA_X$-ADA_2 at 20 °C.

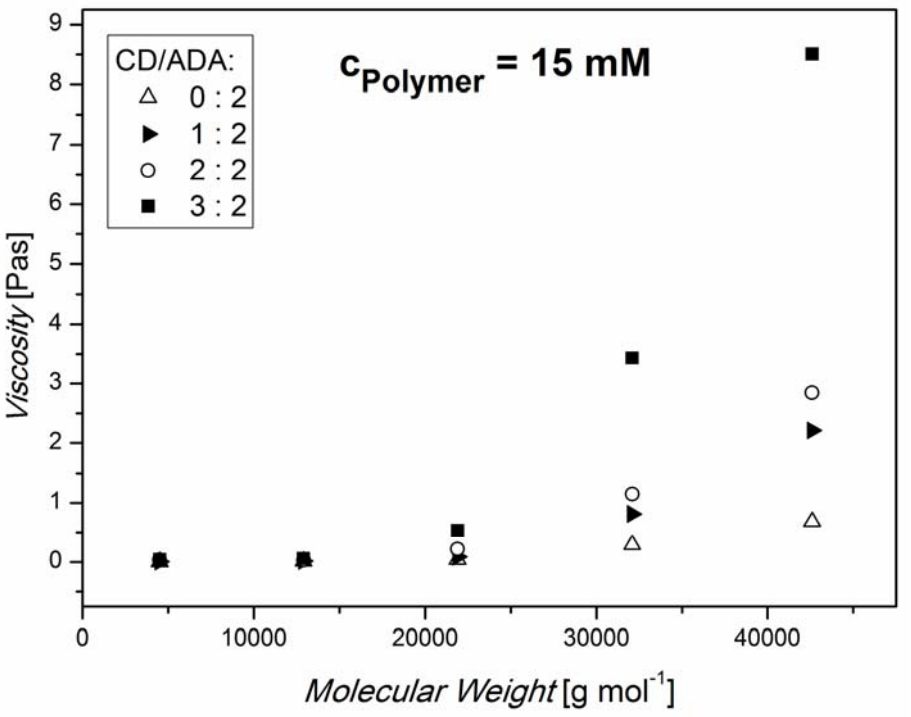

Figure S15. Viscosity values in Pas for $c_{Polymer}$ = 15 mM and different CD/ADA ratios depending on the molecular weight of $PDMA_X$-ADA_2 at 20 °C.

References

1. R. Dong, Y. Liu, Y. Zhou, D. Yan and X. Zhu, *Polym. Chem.*, 2011, **2**, 2771-2774.

2. B. V. K. J. Schmidt, T. Rudolph, M. Hetzer, H. Ritter, F. H. Schacher and C. Barner-Kowollik, *Polym. Chem.*, 2012, **3**, 3139-3145.