Supporting Information:

Synthesis of Redox-Responsive Core-Shell Nanoparticles: Insights into Core-Crosslinking Efficiency

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Table S1. Analytical results of the nanoparticles **NP1.1-12** determined by SEC and DLS, synthesized from **P1**.

[a)] determined by DLS measurements (c = 1 mg/mL); [b)] determined by SEC, measured in DMF + 5 g/L LiBr (PMMA standard) (c = 3 mg/mL). [c)] determined by SEC with non-crosslinked polymer as

NP	eq. cystamine	T [°C]	t [h]	d_h [a)] (H_2O) [nm] (PDI)	d_h [a)] (MeOH) [nm] (PDI)	M_n [b)] [g/mol]	Đ [b)]	cross.[b)] [%]	cross.[c)] [%]
NP1.1	0.5	40	20	18 ± 1 (0.186 ± 0.021)	23 ± 3 (0.091 ± 0.019)	250 500	1.44	83	78
NP1.2	0.5 (HDA)	40	20	17 ± 2 (0.156 ± 0.017)	20 ± 2 (0.226 ± 0.011)	215 800	1.65	79	77
NP1.3	0.5	22	20	17 ± 2 (0.249 ± 0.014)	27 ± 2 (0.198 ± 0.008)	329 100	2.04	82	78
NP1.4	0.5	60	20	129 ± 20* (0.279 ± 0.020)	613 ± 101* (0.168 ± 0.031)	1 117 000	2.45	82	79
NP1.5	0.5	80	20	114 ± 22* (0.291 ± 0.016)	311 ± 31* (0.134 ± 0.070)	---	---	0	79
NP1.6	0.125	40	20	19 ± 1 (0.182 ± 0.026)	290 ± 249 (0.407 ± 0.202)	---	---	20	21
NP1.7	0.25	40	20	35 ± 5 (0.280 ± 0.034)	17 ± 3 (0.152 ± 0.029)	125 000	1.85	61	59
NP1.8	1	40	20	19 ± 3 (0.182 ± 0.026)	19 ± 4 (0.240 ± 0.026)	250 300	1.91	85	81
NP1.9	2	40	20	26 ± 8* (0.280 ± 0.069)	22 ± 4* (0.258 ± 0.040)	278 500	2.40	56	84
NP1.10	5	40	20	17 ± 3* (0.338 ± 0.086)	171 ± 83* (0.305 ± 0.093)	1 430 700	1.87	6	66
NP1.11	0.5	40	48	20 ± 2 (0.193 ± 0.010)	18 ± 3 (0.171 ± 0.010)	223 100	1.58	84	79
NP1.12	0.5	40	72	21 ± 3 (0.168 ± 0.026)	23 ± 1 (0.158 ± 0.032)	217 600	1.54	83	79

reference; *poorly soluble

Table S2. Analytical results of the nanoparticles **NP2.1-NP2.10** determined by SEC and DLS, synthesized from **P2.1-10**.

NP	polymer	DP x/y/z (theo.)	d_h [a] (H_2O) [nm] (PDI)	d_h [a] (MeOH) [nm] (PDI)	M_n [b] [g/mol]	Đ [b]	cross.[b] [%]	cross.[c] [%]
NP2.1	P2.1	51/0/5 (51/0/5)	13 ± 3 (0.307 ± 0.070)	13 ± 2 (0.231 ± 0.057)	115 500	1.42	37	49
NP2.2	P2.2	51/0/10 (51/0/10)	14 ± 3 (0.298 ± 0.035)	14 ± 2 (0.274 ± 0.071)	174 600	2.00	76	78
NP2.3	P2.3	51/0/14 (51/0/15)	20 ± 3 (0.207 ± 0.010)	30 ± 4 (0.228 ± 0.009)	287 700	2.14	85	84
NP2.4	P2.4	51/0/20 (51/0/20)	40 ± 5* (0.284 ± 0.063)	128 ± 23* (0.321 ± 0.009)	387 600	2.42	85	86
NP2.5	P2.5	51/5/5 (51/5/5)	21 ± 2 (0.197 ± 0.019)	17 ± 2 (0.191 ± 0.025)	150 800	1.30	67	65
NP2.6	P2.6	51/5/10 (51/5/10)	22 ± 1 (0.216 ± 0.018)	22 ± 1 (0.180 ± 0.016)	183 200	1.45	81	80
NP2.7	P2.7	51/6/15 (51/5/15)	48 ± 15* (0.297 ± 0.039)	69 ± 14* (0.323 ± 0.028)	428 300	3.04	83	83
NP2.8	P2.8	51/9/5 (51/10/5)	22 ± 3 (0.207 ± 0.042)	16 ± 2 (0.311 ± 0.022)	129 800	1.52	52	62
NP2.9	P2.9	51/11/10 (51/10/10)	25 ± 2 (0.212 ± 0.009)	25 ± 2 (0.181 ± 0.005)	306 400	2.05	83	82
NP2.10	P2.10	51/10/14 (51/10/15)	68 ± 19* (0.327 ± 0.044)	637 ± 94* (0.115 ± 0.064)	392 200	2.69	86	88

a) determined by DLS measurements (c = 1 mg/mL); b) determined by SEC, measured in DMF + 5 g/L LiBr (PMMA standard) (c = 3 mg/mL); c) determined by SEC with non-crosslinked polymer as reference; *: poorly soluble.

Table S3. Results of the SEC recovery experiments for **P1** and **NP1.1**.

polymer/NP	recovery [a] [%]	S.D. [a] [%]
P1	90	3
NP1.1	92	4

a) determined by SEC, measured in DMF + 5 g/L LiBr (PMMA standard) (c = 3 mg/mL) n = 3.

Table S4. Hydrodynamic diameters (d_h) and polydispersity indices (PDI) of the nanoparticles NP3.1-NP3.8 synthesized from the precursor polymer **P2.11** with the different amine crosslinkers (**V1-V6**). Determined by DLS measurements in water and methanol (β = 1 mg/mL, at 25 °C).

crosslinker	nanoparticle	d_h (H_2O) (nm)	PDI	d_h (MeOH) (nm)	PDI
1,4-diamino butane (**V1**)	**NP3.1**	16 ± 1	0.19 ± 0.02	22 ± 1	0.23 ± 0.02
1,6-diamino hexane (**V2**)	**NP3.2**	12 ± 3	0.25 ± 0.06	14 ± 2	0.23 ± 0.05
cystamine (**V3**)	**NP3.3**	19 ± 1	0.15 ± 0.03	19 ± 1	0.15 ± 0.03
1,8-diamino oktane (**V4**)	**NP3.4**	16 ± 2	0.20 ± 0.02	23 ± 2	0.22 ± 0.02
4,4‘-diamino diphenylmethan (**V5**)	**NP3.5**	18 ± 1	0.15 ± 0.03	1 ± 1	0.59 ± 0.20
	NP3.6 [a]	19 ± 2	0.22 ± 0.02	2 ± 2	0.27 ± 0.05
tris(2-amino-ethyl)amine (**V6**)	**NP3.7** [b]	15 ± 2	0.16 ± 0.02	19 ± 2	0.14 ± 0.03
	NP3.8	18 ± 3	0.16 ± 0.05	16 ± 4	0.20 ± 0.01

[a] Use of 1.00 eq. or 0.99 eq. of the crosslinker 4,4'-diamino-diphenylmethane (V5). [b] Use of 0.33 eq. of the crosslinker tris(2-aminoethyl)amine (V6). 0.5 eq. of each of the other cross-linkers were used.

Table S5. Hydrodynamic diameters (dh) and polydispersity indices (PDI) of the nanoparticles NP7.1-NP12.4 synthesized from the precursor polymer **P2.12** with the different amine crosslinkers (V1-V6). Determined by DLS measurements in water and methanol (β = 1 mg/mL, at 25 °C).

crosslinker	nanoparticle	d_h (H_2O) (nm)	PDI	d_h (MeOH) (nm)	PDI
1,4-diamino butane (**V1**)	**NP4.1**	21 ± 2	0.17 ± 0.03	24 ± 2	0.16 ± 0.03
1,6-diamino hexane (**V2**)	**NP4.2**	16 ± 2	0.23 ± 0.03	23 ± 1	0.16 ± 0.02
cystamine (**V3**)	**NP4.3**	20 ± 2	0.19 ± 0.02	22 ± 4	0.14 ± 0.02
1,8-diamino oktane (**V4**)	**NP4.4**	18 ± 2	0.18 ± 0.02	23 ± 3	0.21 ± 0.02
4,4‘-diamino diphenylmethan (**V5**)	**NP4.5**	20 ± 1	0.15 ± 0.04	2 ± 2	0.52 ± 0.13
	NP4.6 [a]	21 ± 1	0.20 ± 0.03	1.0 ± 0.3	0.51 ± 0.21
tris(2-amino-ethyl)amine (**V6**)	**NP4.7** [b]	21 ± 2	0.16 ± 0.03	22 ± 3	0.15 ± 0.03
	NP4.8	21 ± 1	0.17 ± 0.02	21 ± 3	0.19 ± 0.02

The crosslinker **V5** was partially dissolved in [a] toluene (NP4.6, before addition to the polymer solution. [b]Use of 0.33 eq. of the crosslinker tris(2-aminoethyl)amine (**V6**). 0.5 eq. of each of the other cross-linkers were used.

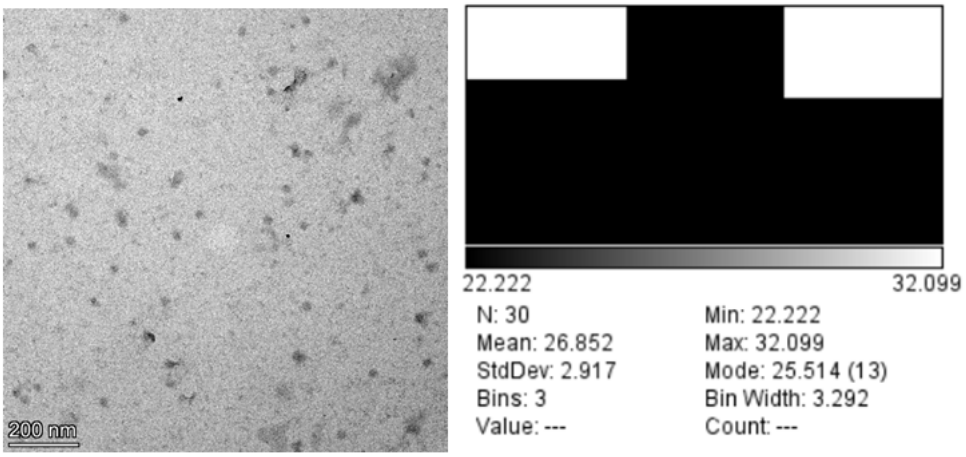


Figure S1. TEM images of **NP1.1** in H_2O (c = 0.01 mg/mL). Stained with uranyl acetate. Mean diameter = 27 ± 3 nm.

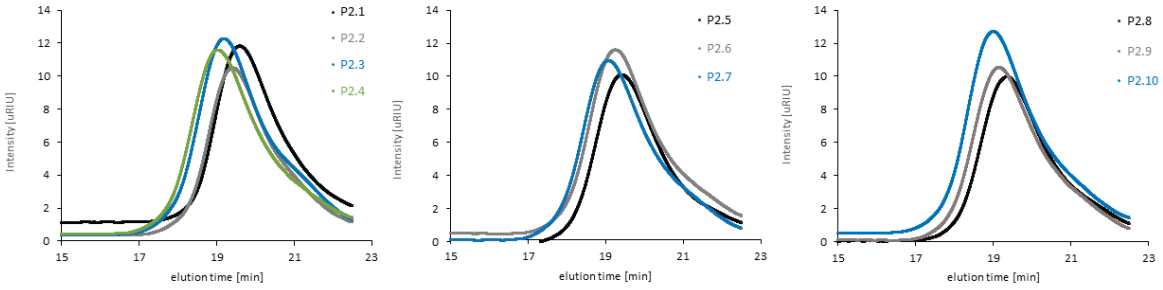


Figure S2. SEC elugrams of **P2.1 - P2.10**.

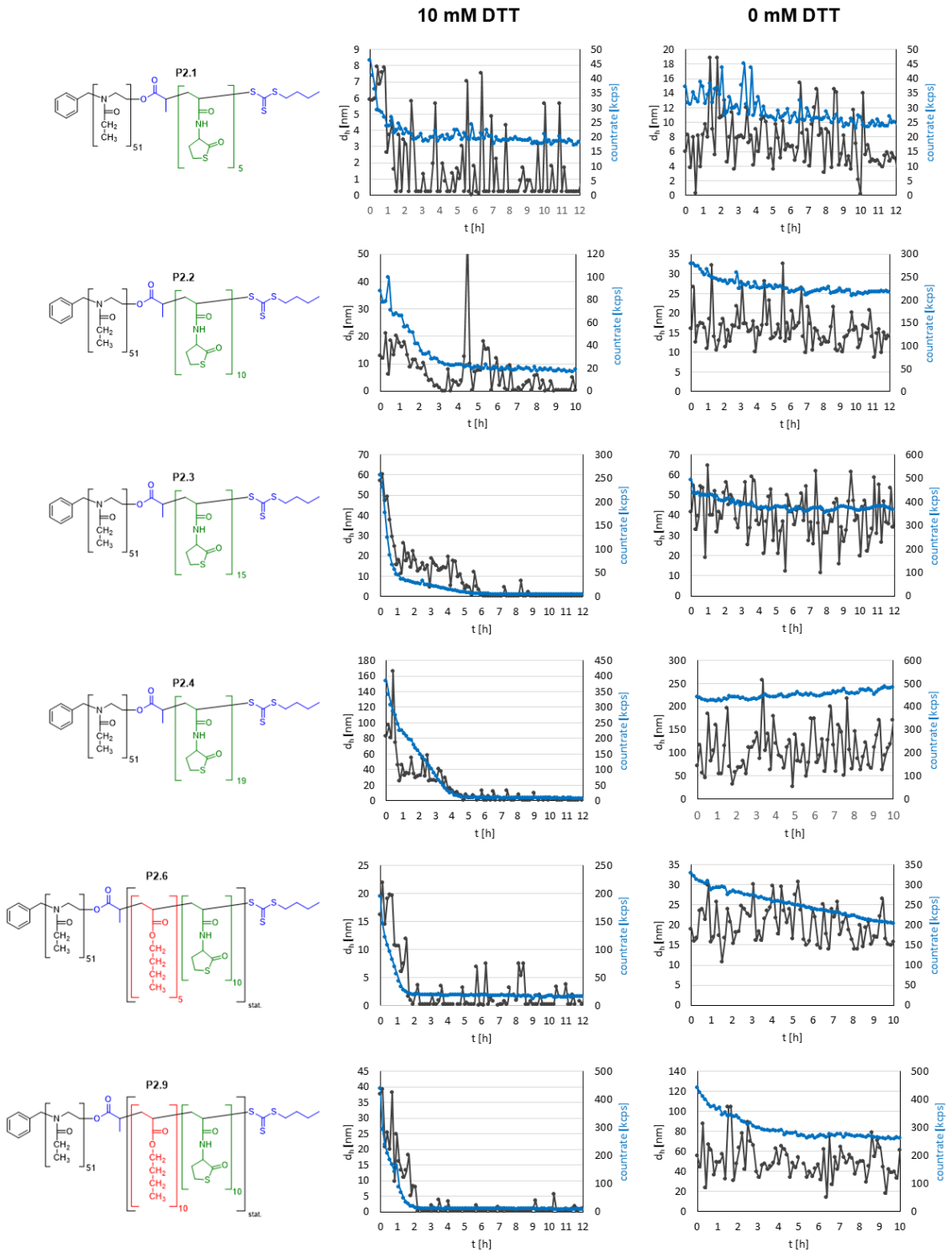


Figure S3. Degradation experiments of **NP2.1 – NP2.9** to analyze the influence of hydrophobic and crosslinkable monomers per polymer chain on the degradation speed monitored *via* DLS. The samples were dissolved in MeOH with 1 %v/v TEA and degassed with Argon for 30 min. Afterwards DTT was added to the solution and the measurement was started. The hydrodynamic diameter is shown in black and the countrate in blue.

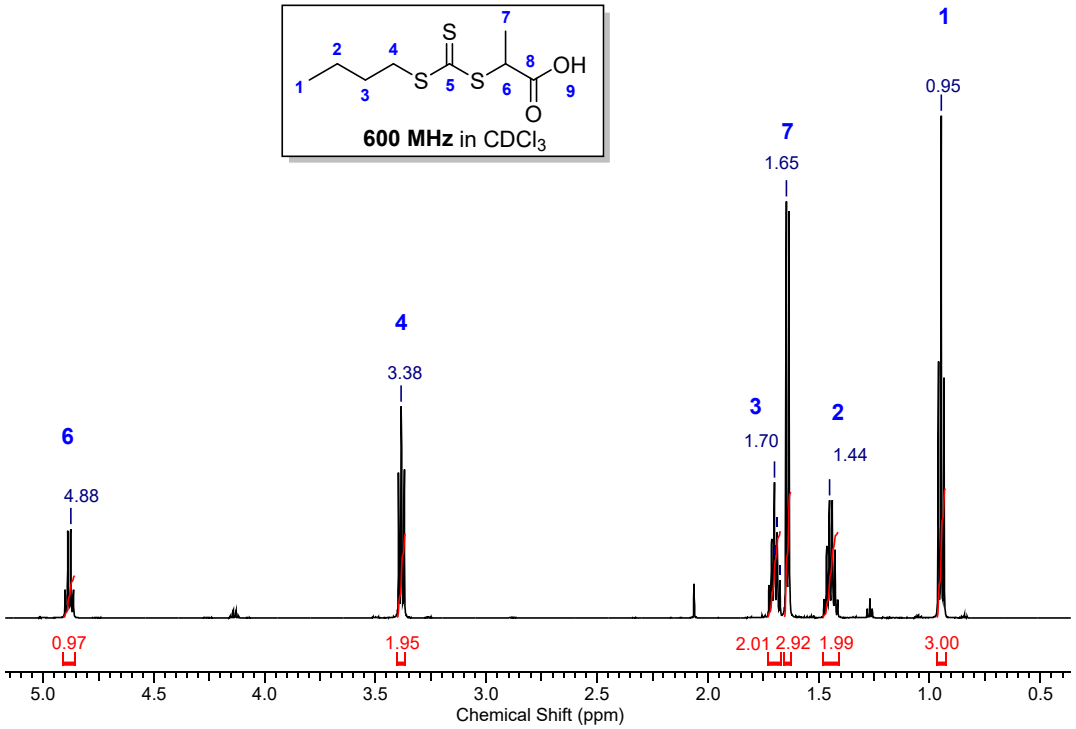


Figure S4: ^{1}H-NMR of **T1** in $CDCl_3$.

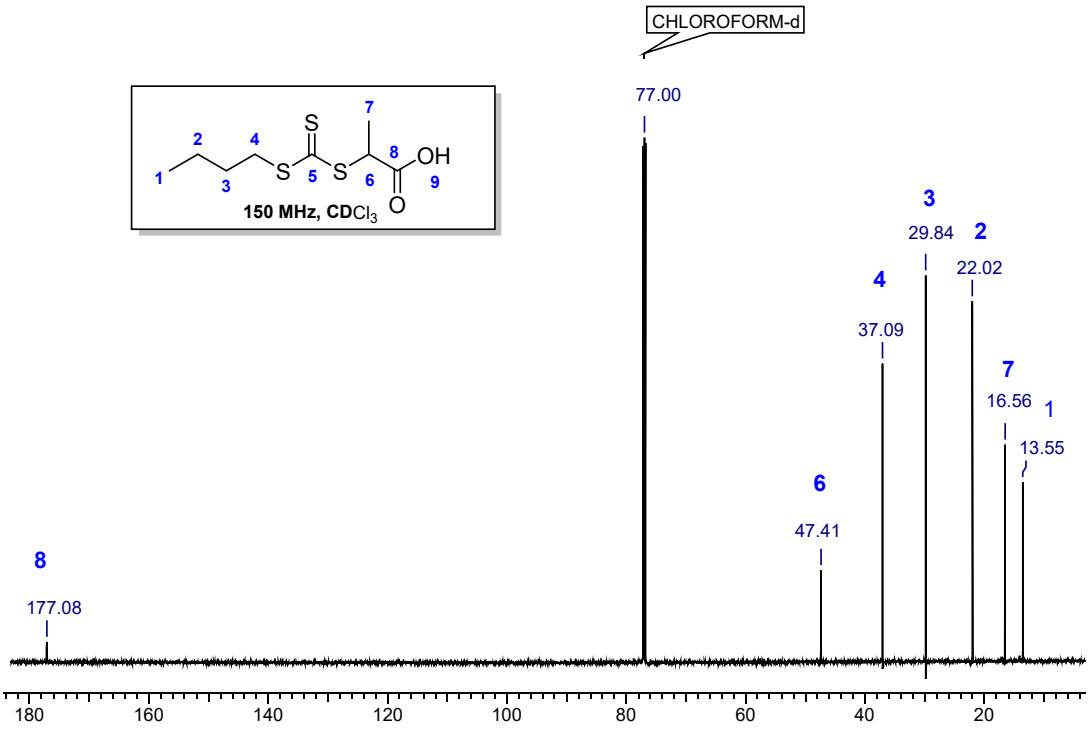


Figure S5: ^{13}C-NMR of **T1** in $CDCl_3$.

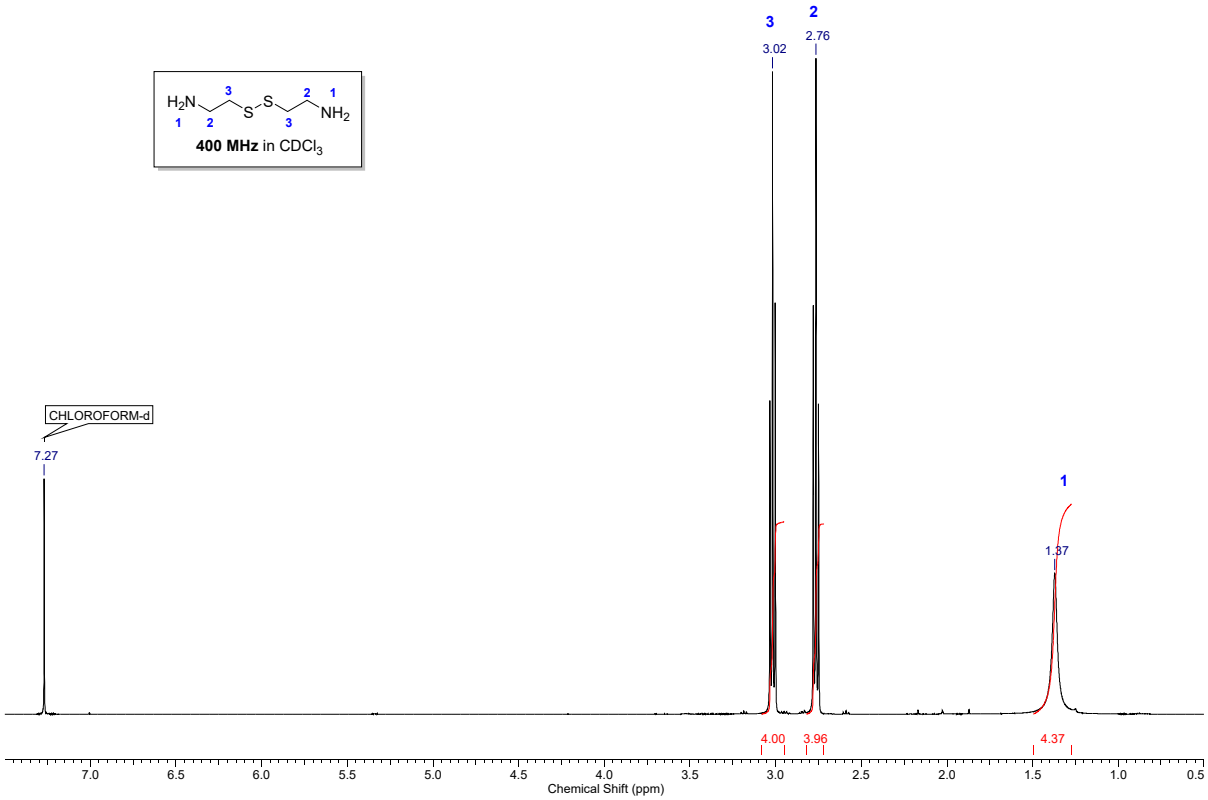


Figure S6: ^{1}H-NMR of cystamine in $CDCl_3$.

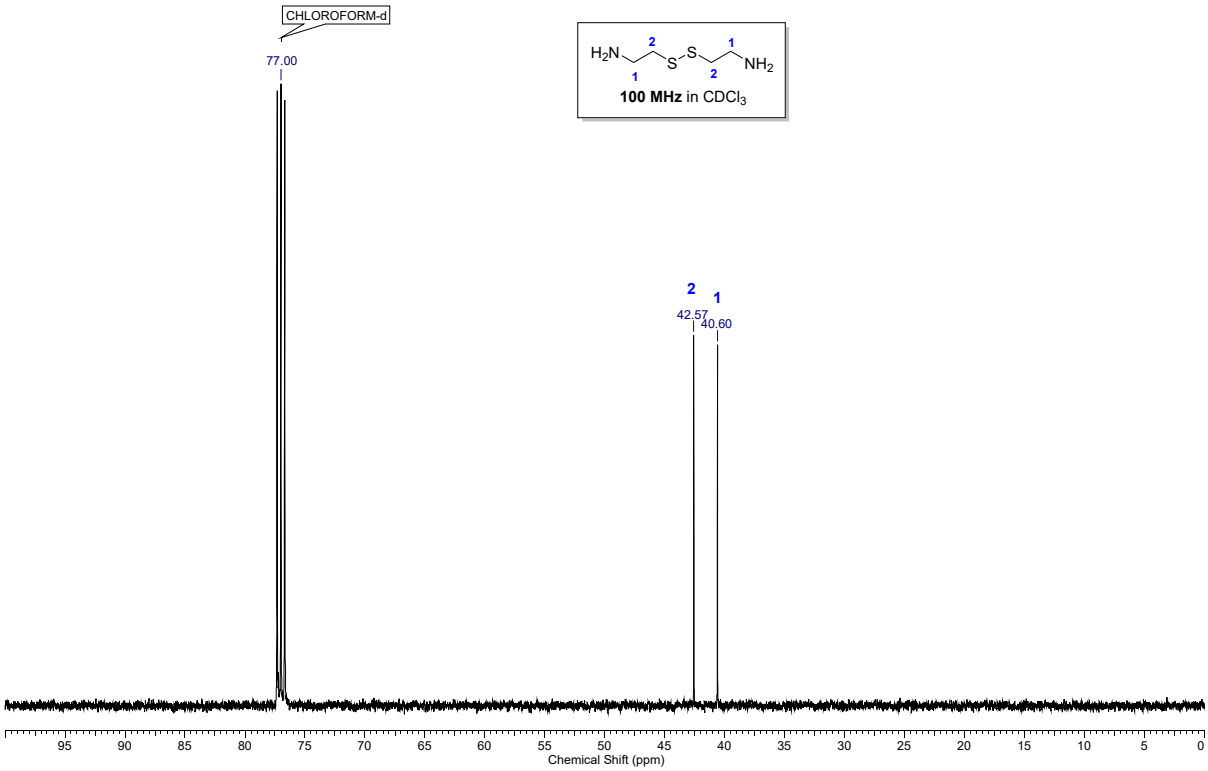


Figure S7: ^{13}C-NMR of cystamine in $CDCl_3$.

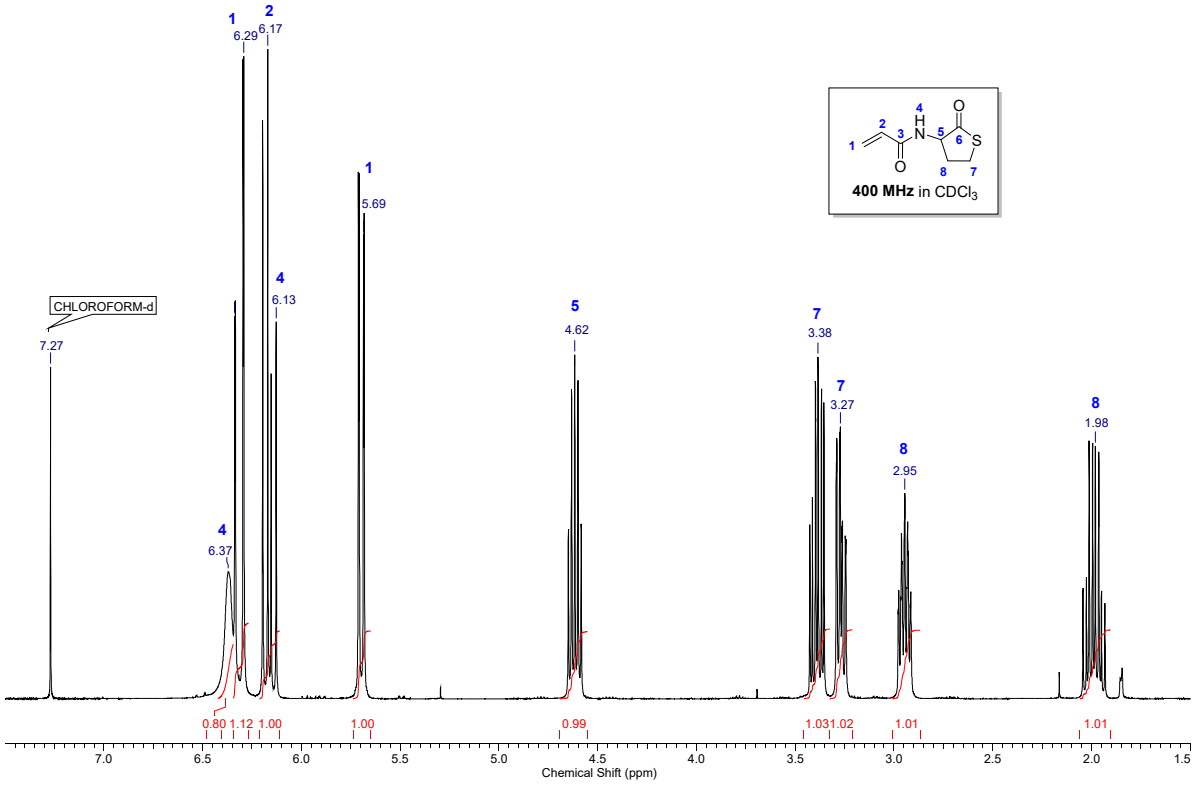


Figure S8: ^{1}H-NMR of **M1** in $CDCl_3$.

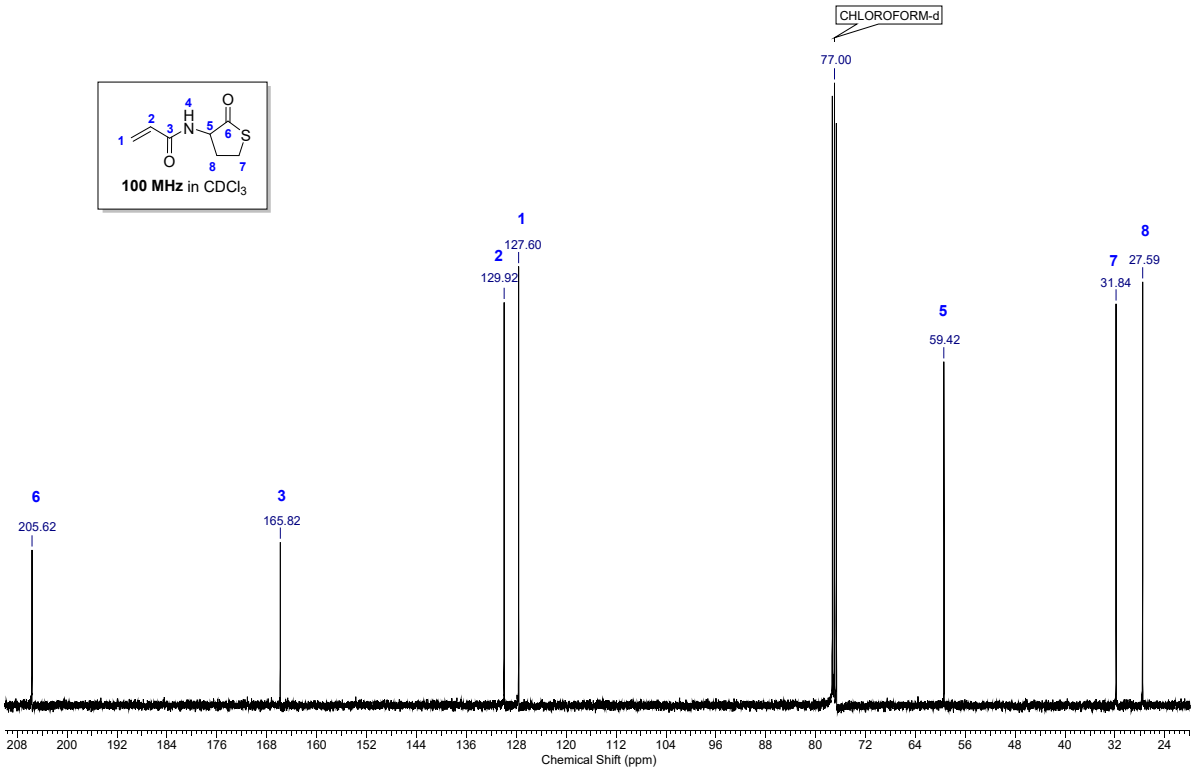


Figure S9: ^{13}C-NMR of **M1** in $CDCl_3$.

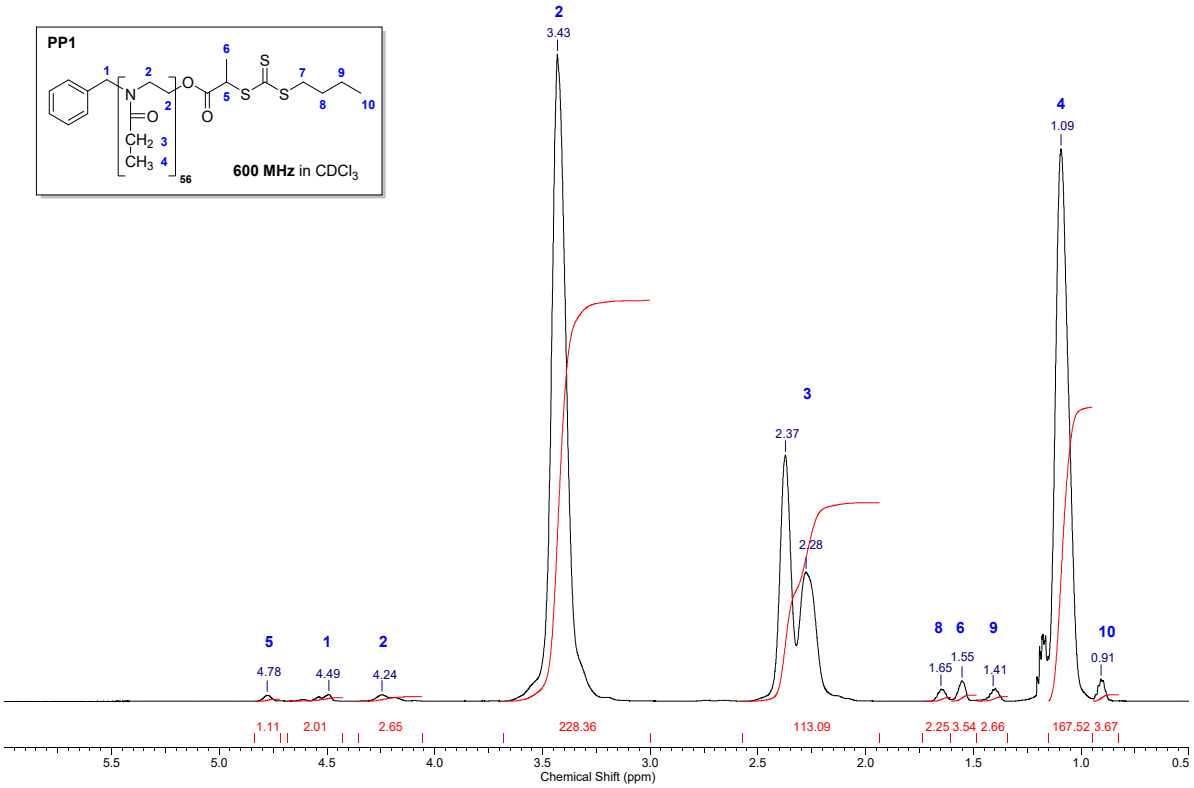


Figure S10: ^{1}H-NMR of **PP1** in $CDCl_3$.

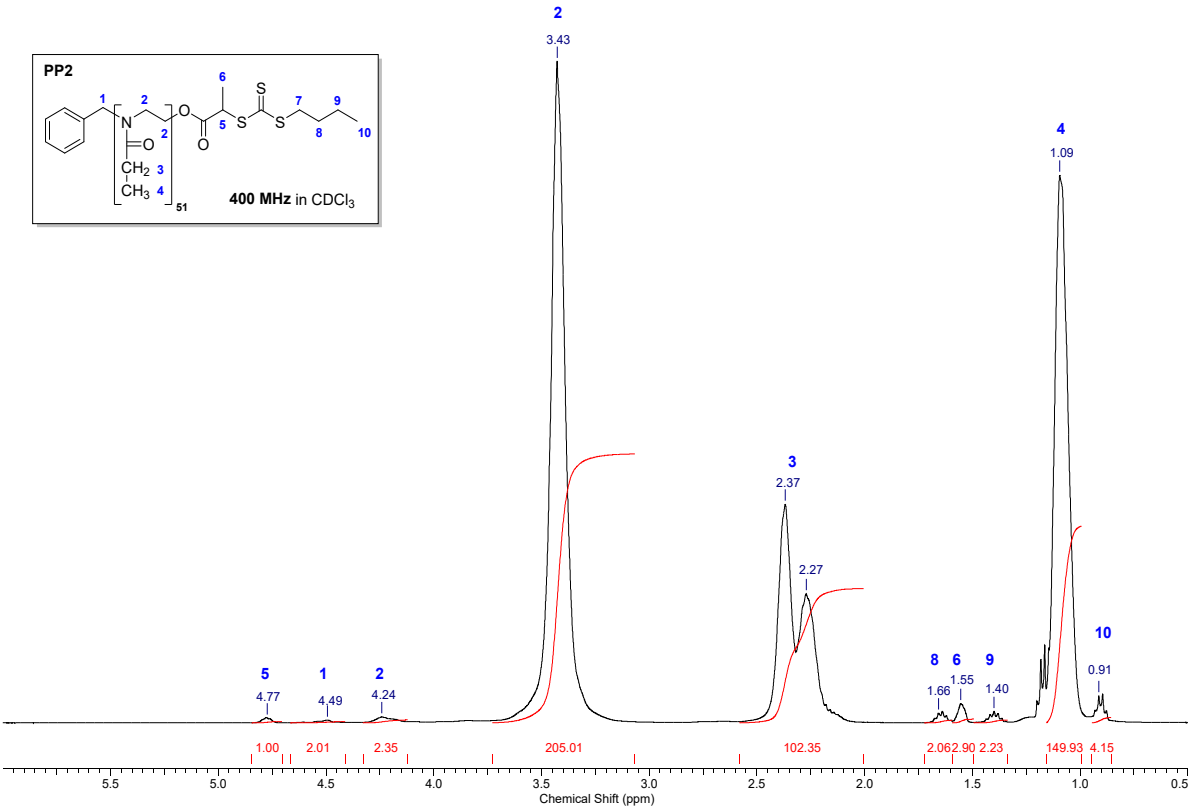


Figure S11: ^{1}H-NMR of **PP2** in $CDCl_3$.

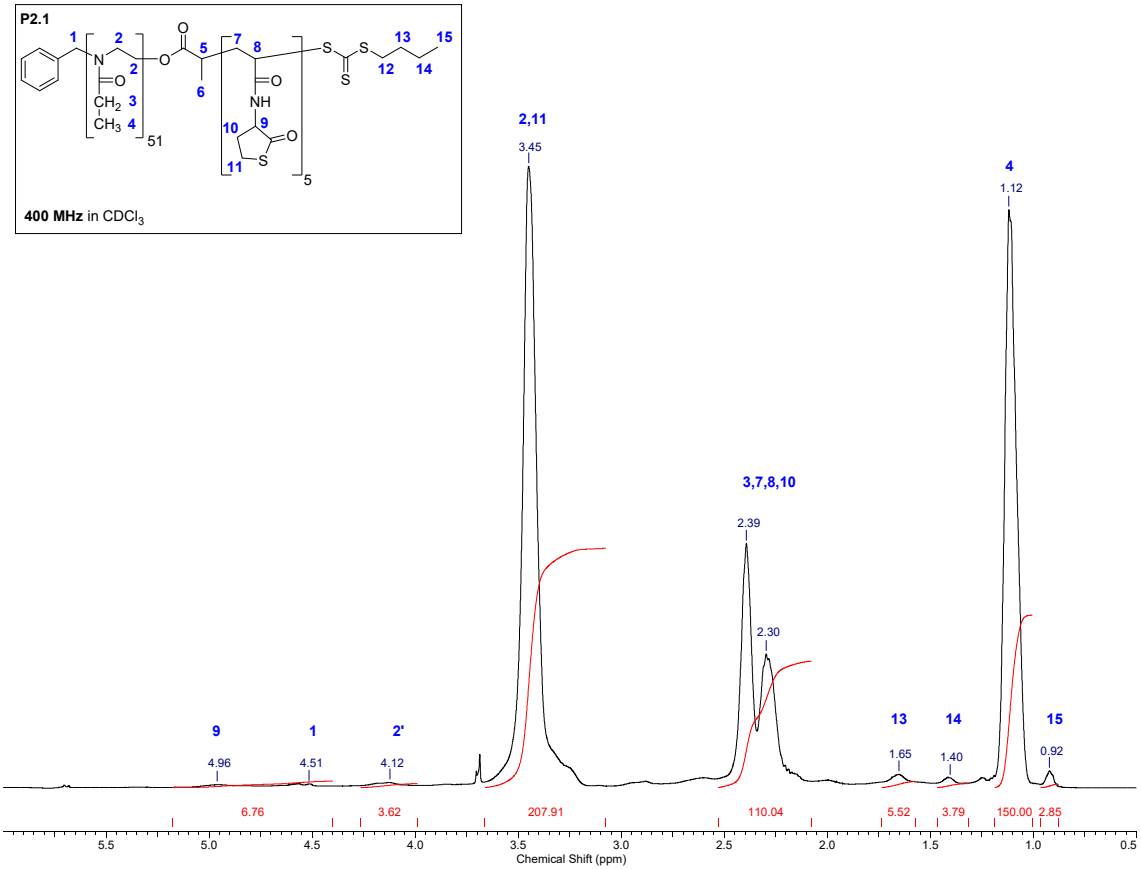


Figure S12: ^{1}H-NMR of **P2.1** in $CDCl_3$.

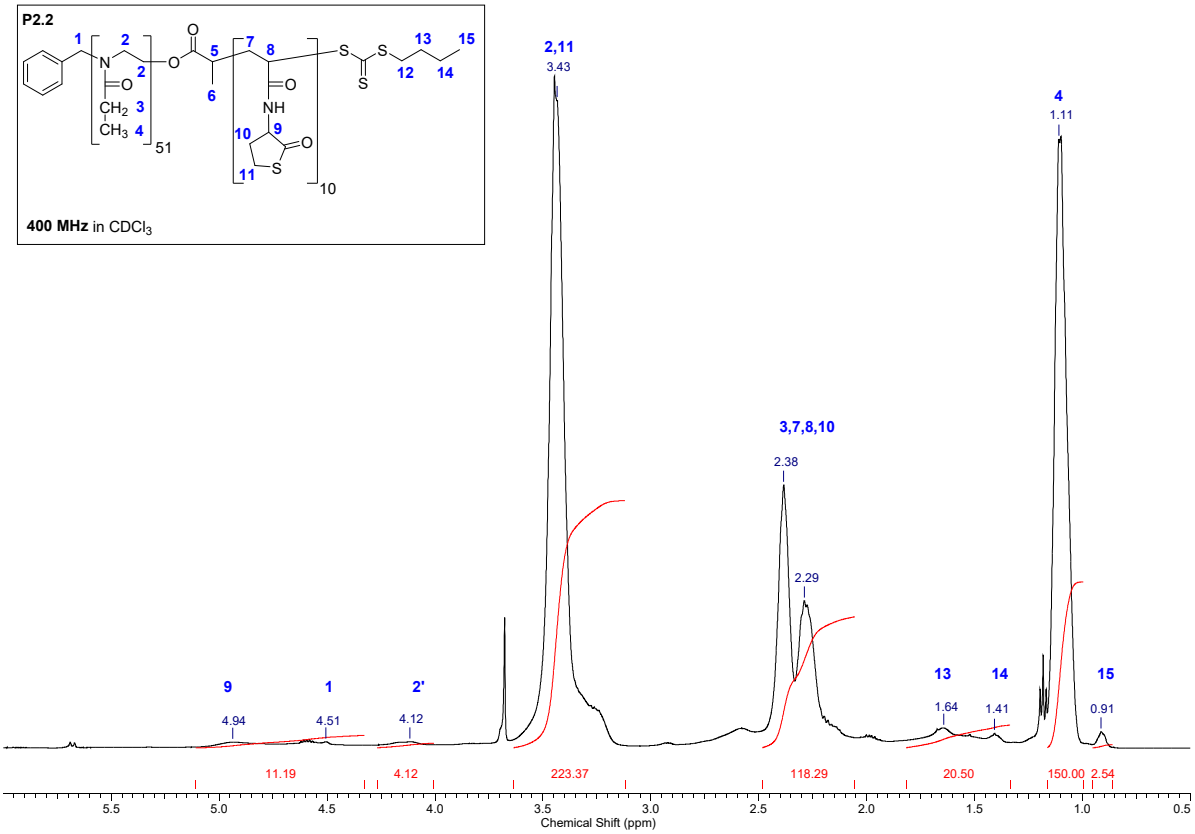


Figure S13: ^{1}H-NMR of **P2.2** in $CDCl_3$.

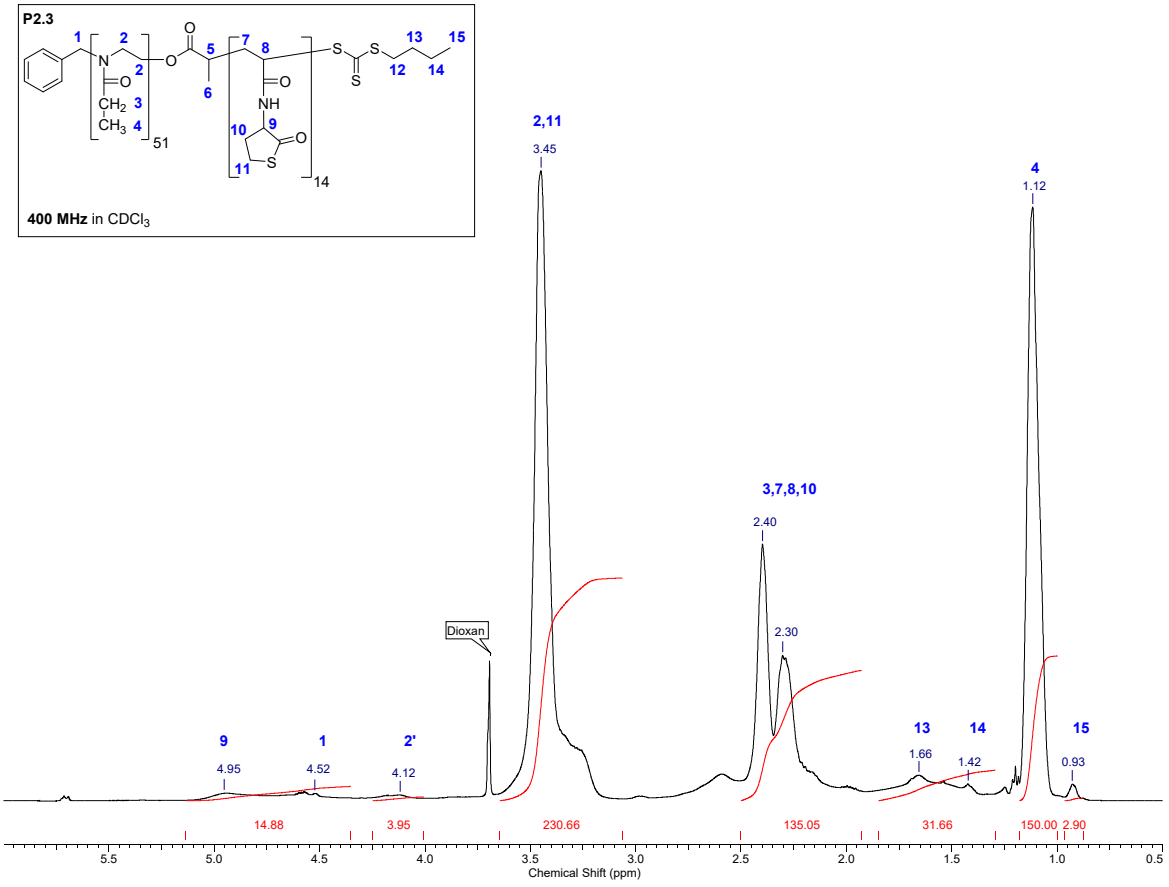


Figure S14: ^{1}H-NMR of **P2.3** in $CDCl_3$.

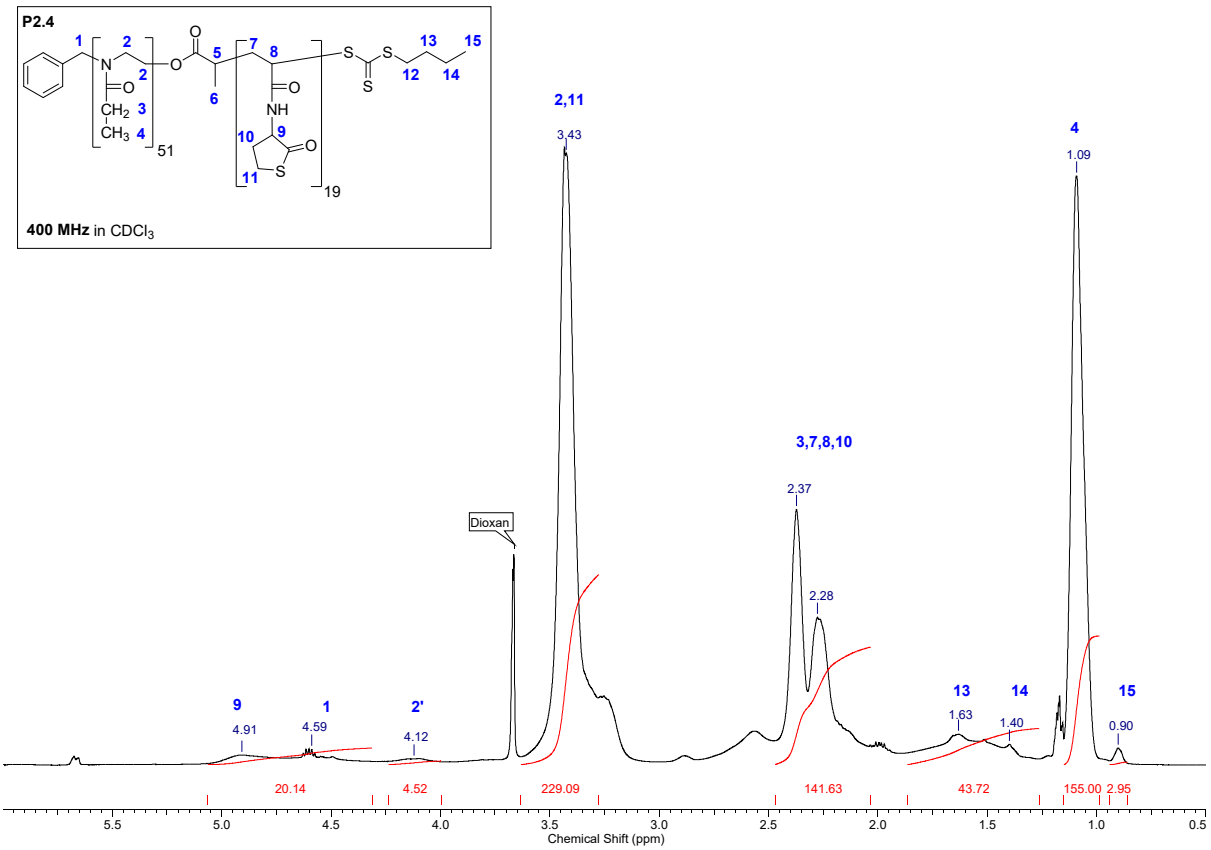


Figure S15: ^{1}H-NMR of **P2.4** in $CDCl_3$.

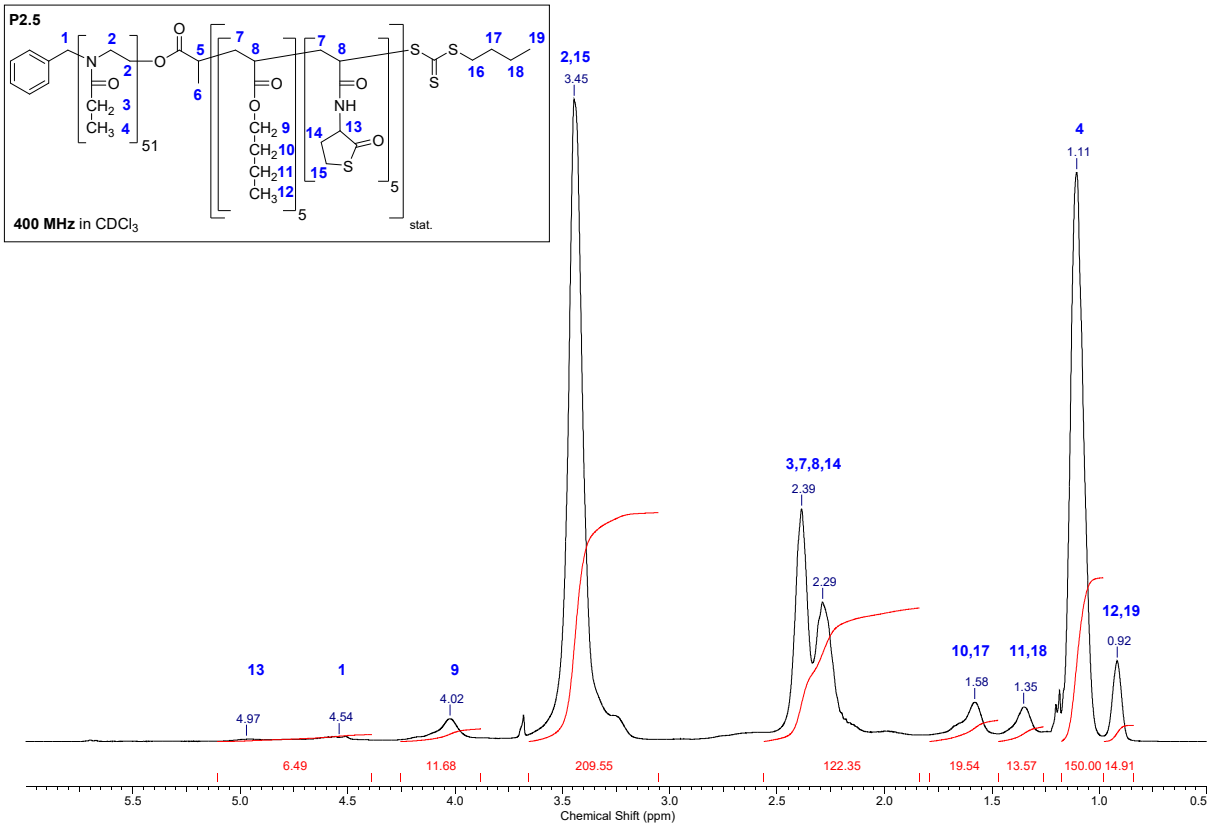


Figure S16: ^{1}H-NMR of **P2.5** in $CDCl_3$.

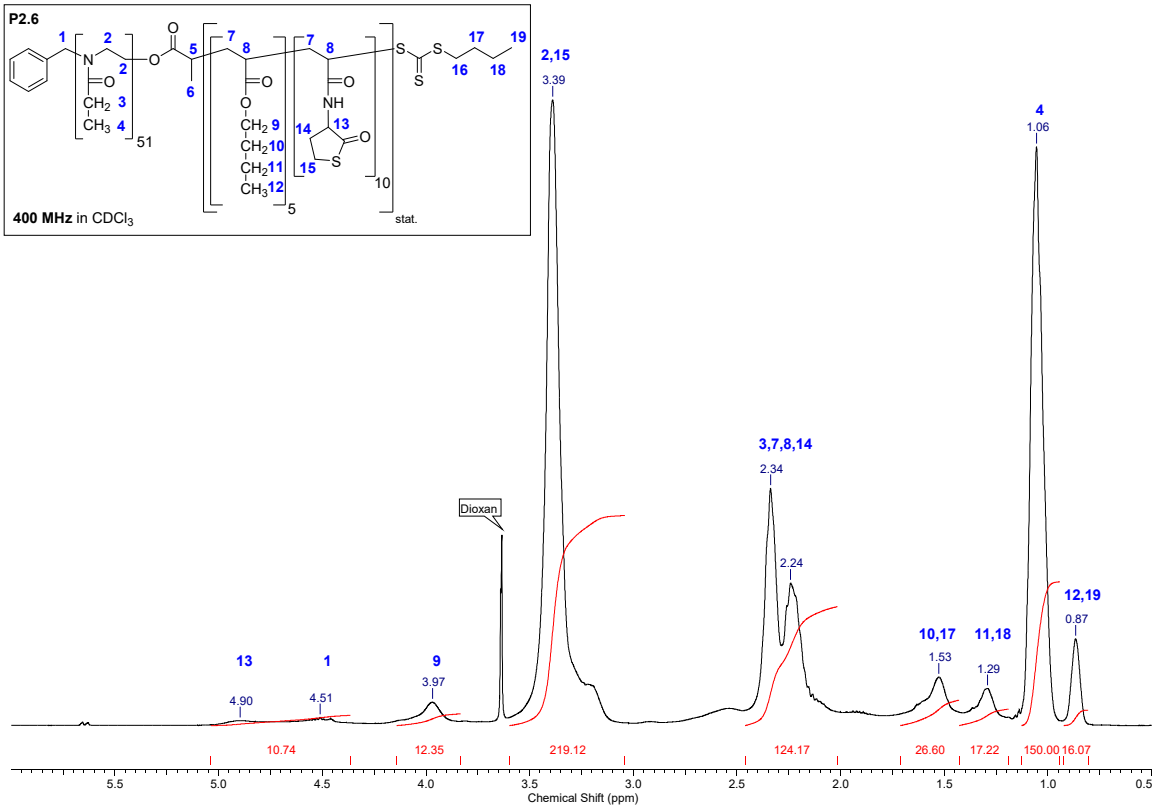


Figure S17: ^{1}H-NMR of **P2.6** in $CDCl_3$.

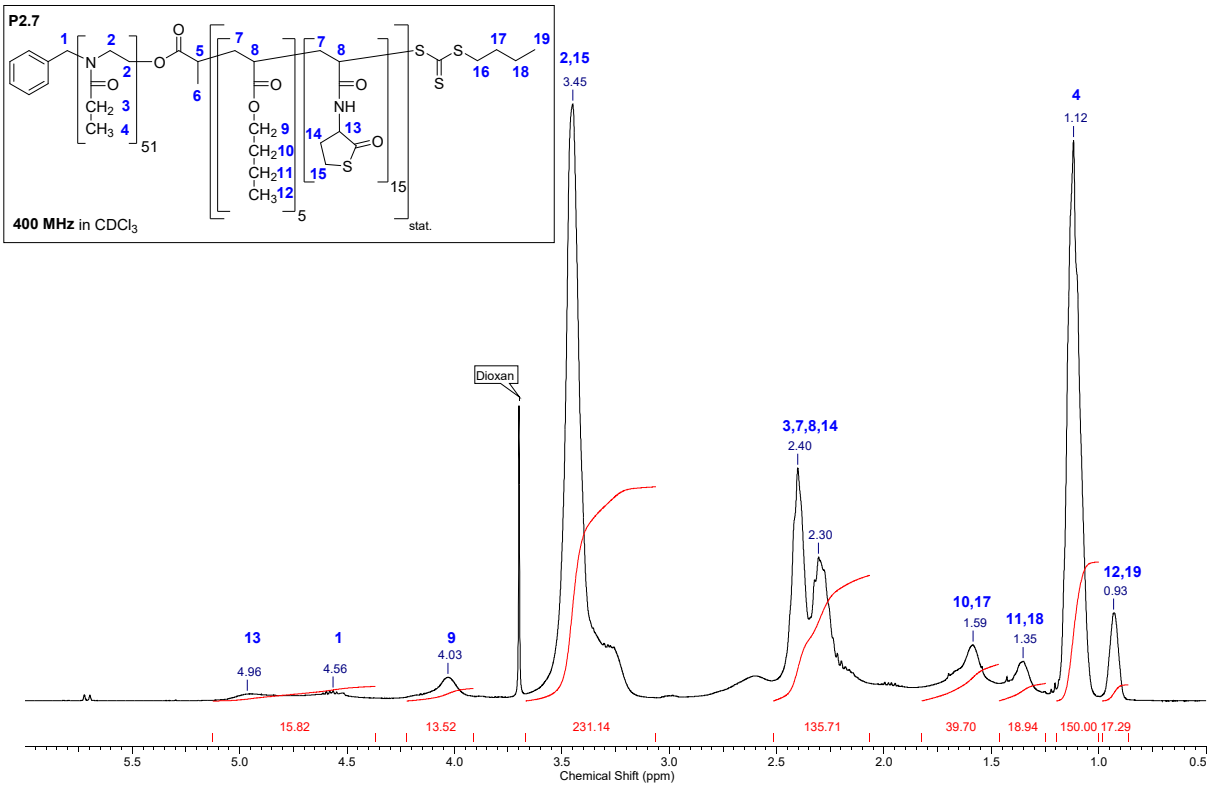


Figure S18: ^{1}H-NMR of **P2.7** in $CDCl_3$.

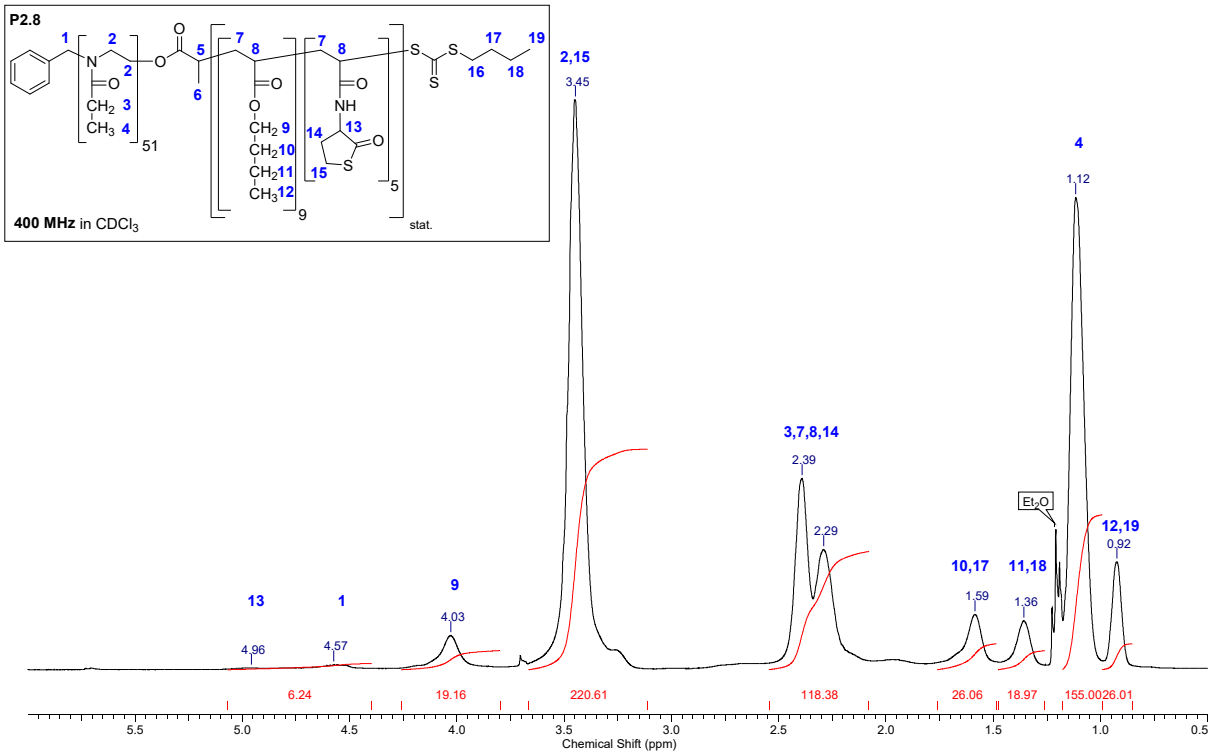


Figure S19: ^{1}H-NMR of **P2.8** in $CDCl_3$.

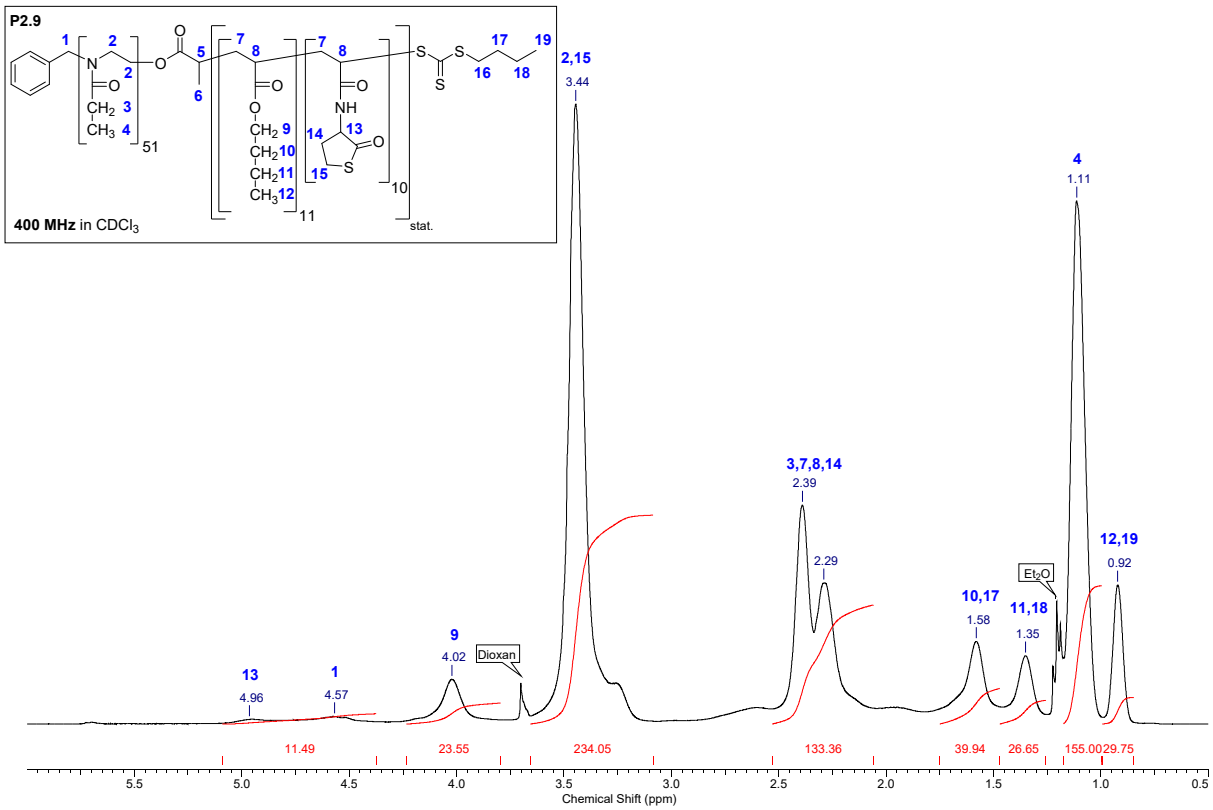


Figure S20: ^{1}H-NMR of **P2.9** in $CDCl_3$.

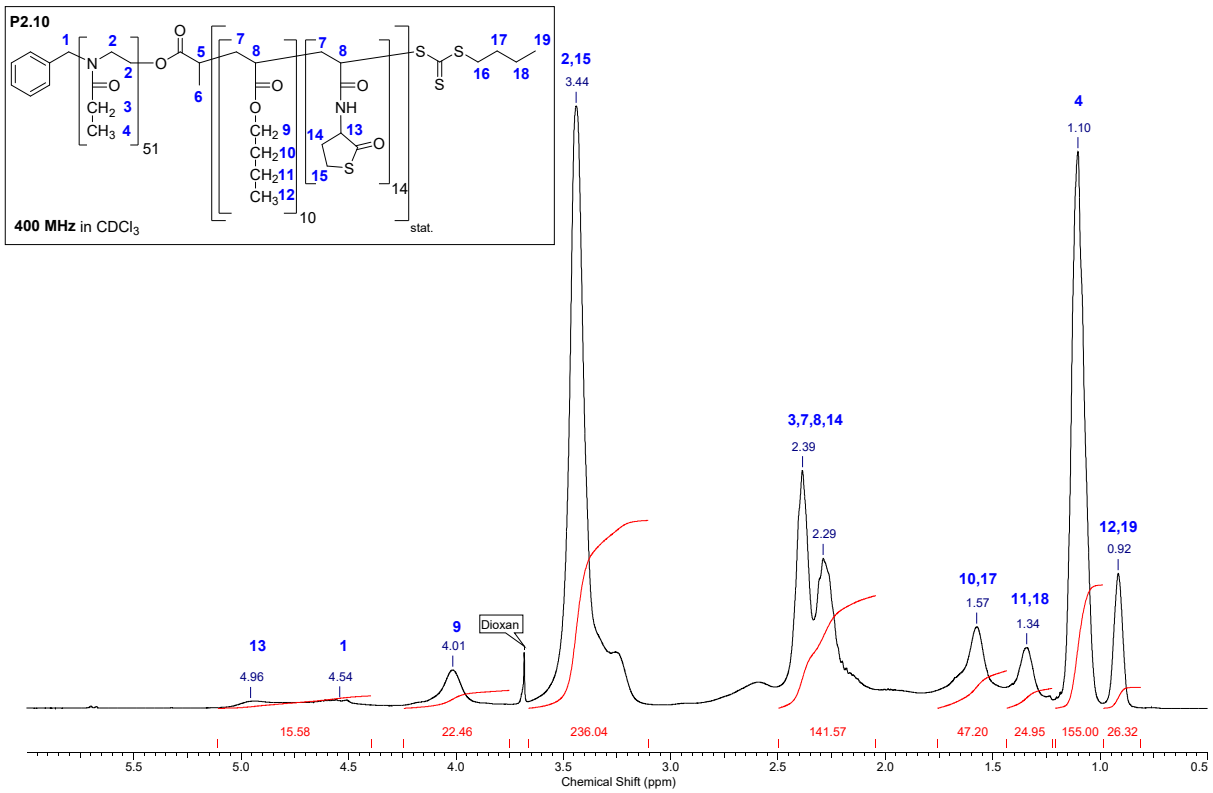


Figure S21: ^{1}H-NMR of **P2.10** in $CDCl_3$.

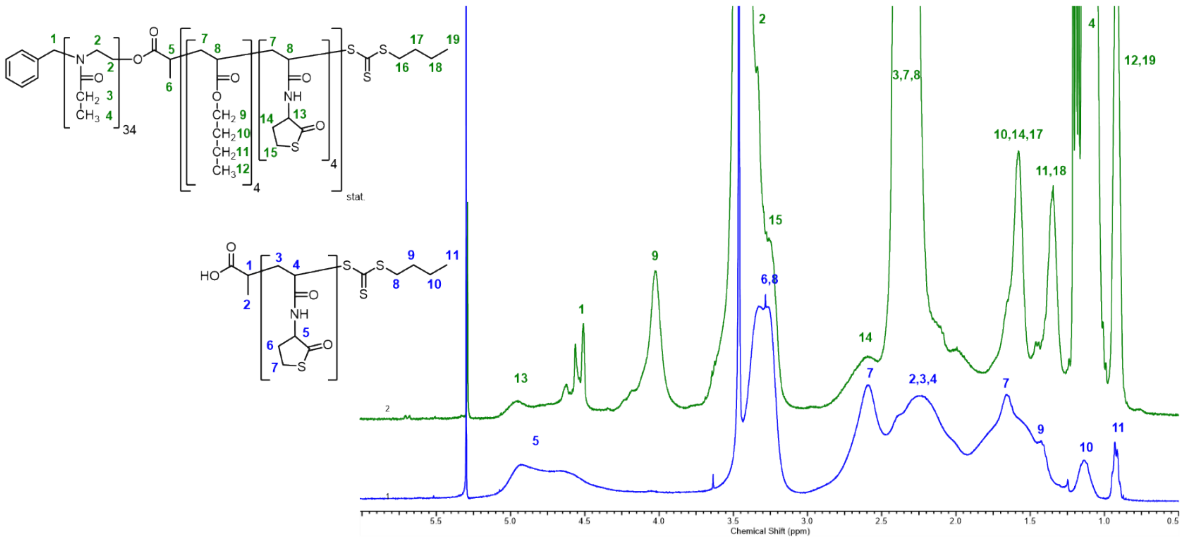


Figure S22. ^{1}H-NMR of the homopolymer poly(thiolactone) and a block copolymer for comparison in $CDCl_3$.

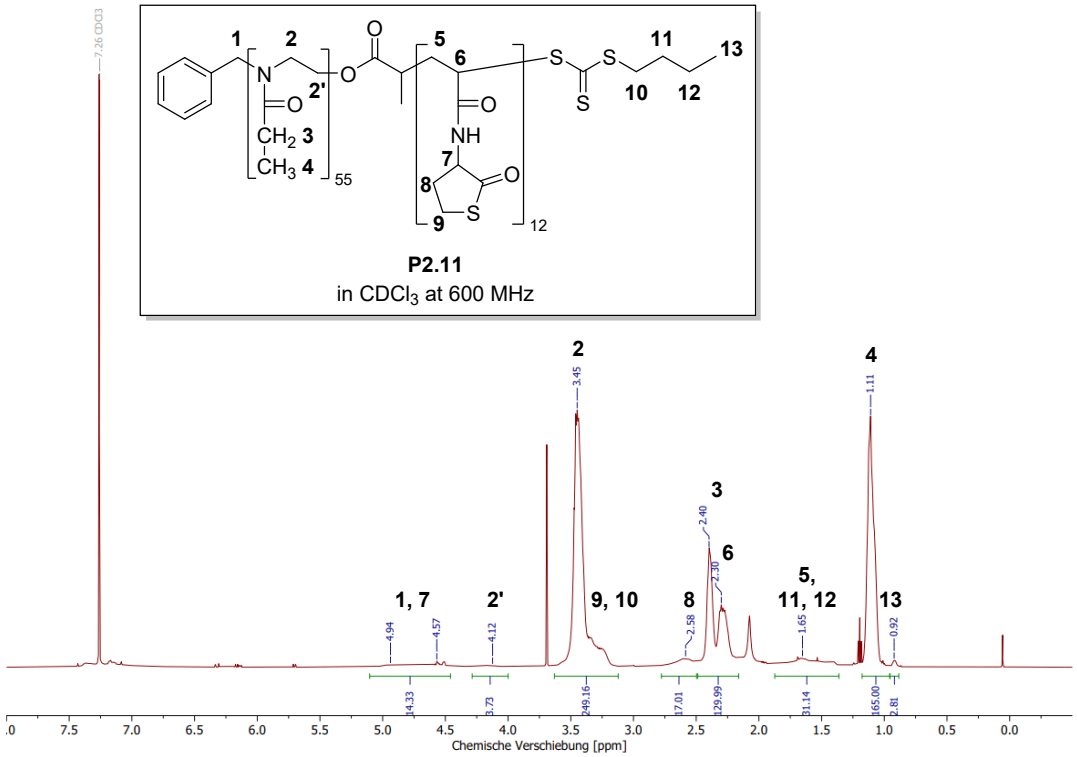


Figure S23. ^{1}H-NMR of the block copolymer **P2.11** in $CDCl_3$.

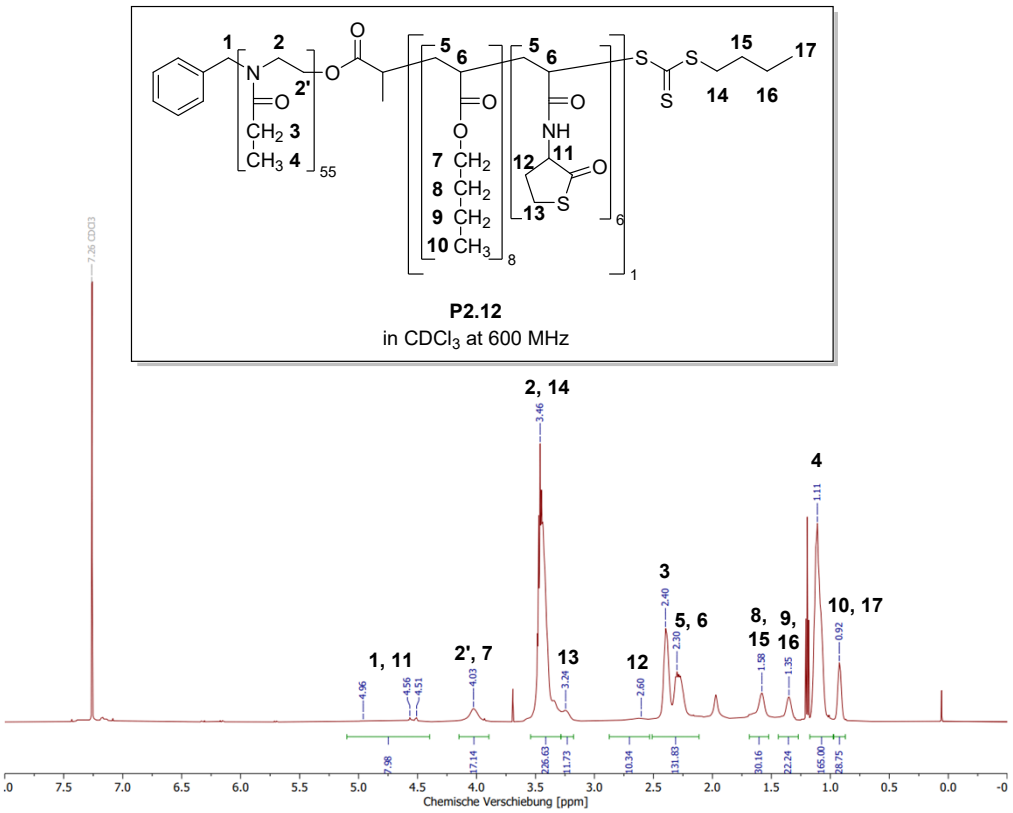
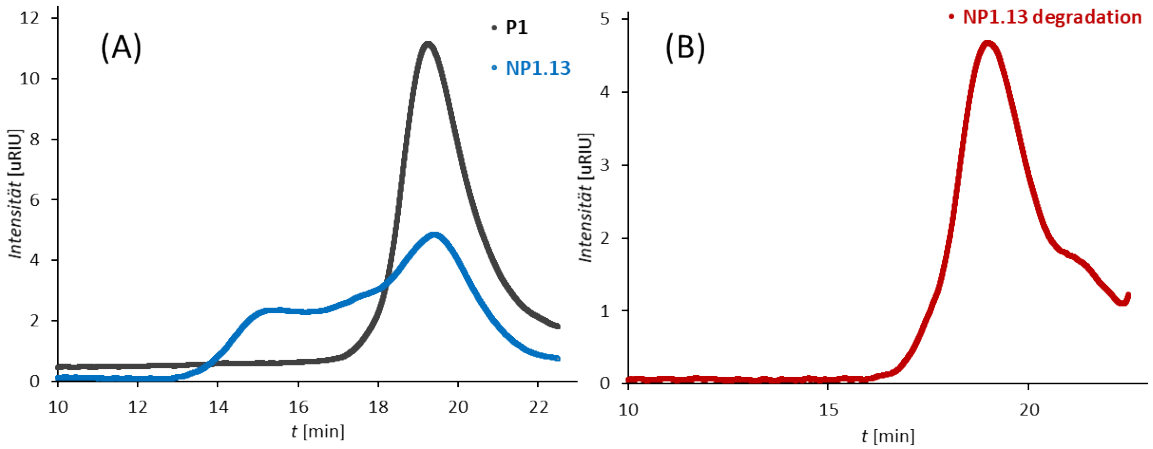


Figure S24. ^{1}H-NMR of the block copolymer **P2.12** in $CDCl_3$.



NP	eq. cystamine	T [°C]	t [h]	d_h[a] (H_2O) [nm] (PDI)	d_h[a] (MeOH) [nm] (PDI)	M_n[b] [g/mol]	Đ [b]	cross.[b] [%]	cross.[c] [%]
NP1.13	0.5(HexA)	40	20	42 ± 14 (0.291 ± 0.019)	19 ± 3 (0.203 ± 0.030)	---	---	26	35

Figure S25. SEC chromatograms of the nanoparticle **NP1.13** from **P1** and 1-hexylamine after 24h reaction time at 40 °C (A) and after degradation for 24 h at 36 °C in PBS-buffer with 10 mM DTT (B).

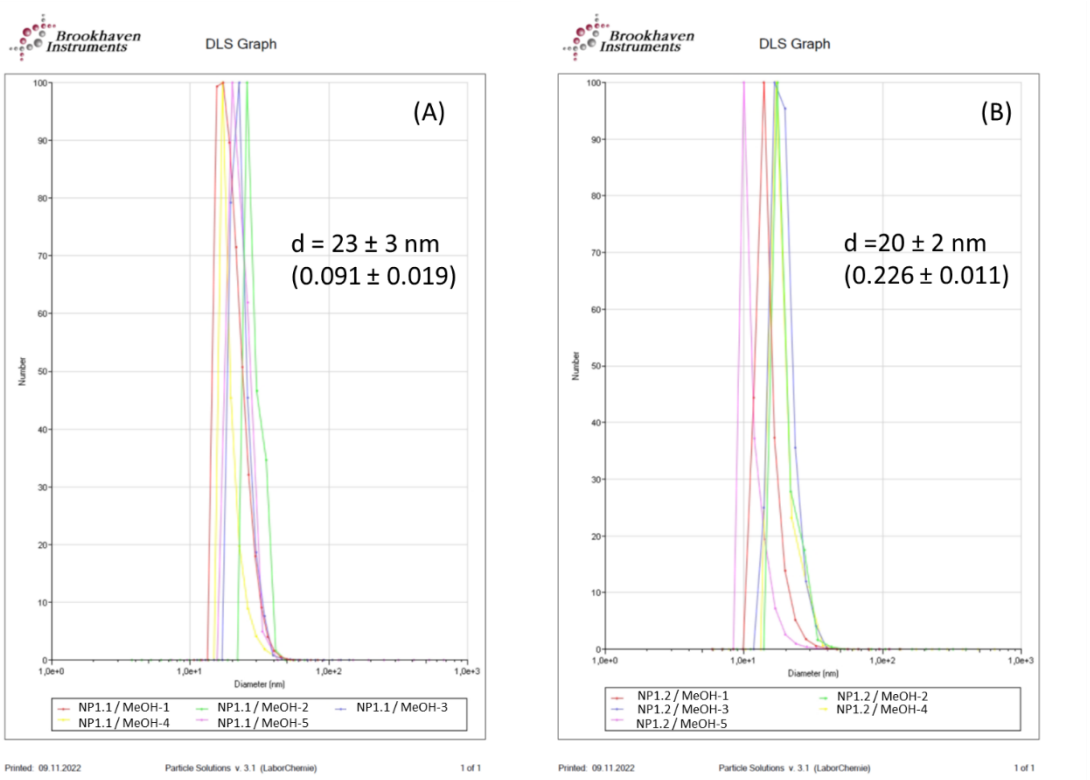


Figure S26. DLS data for NP1.1 (A) and NP1.2 (B) from five measurements in MeOH (by number distribution).

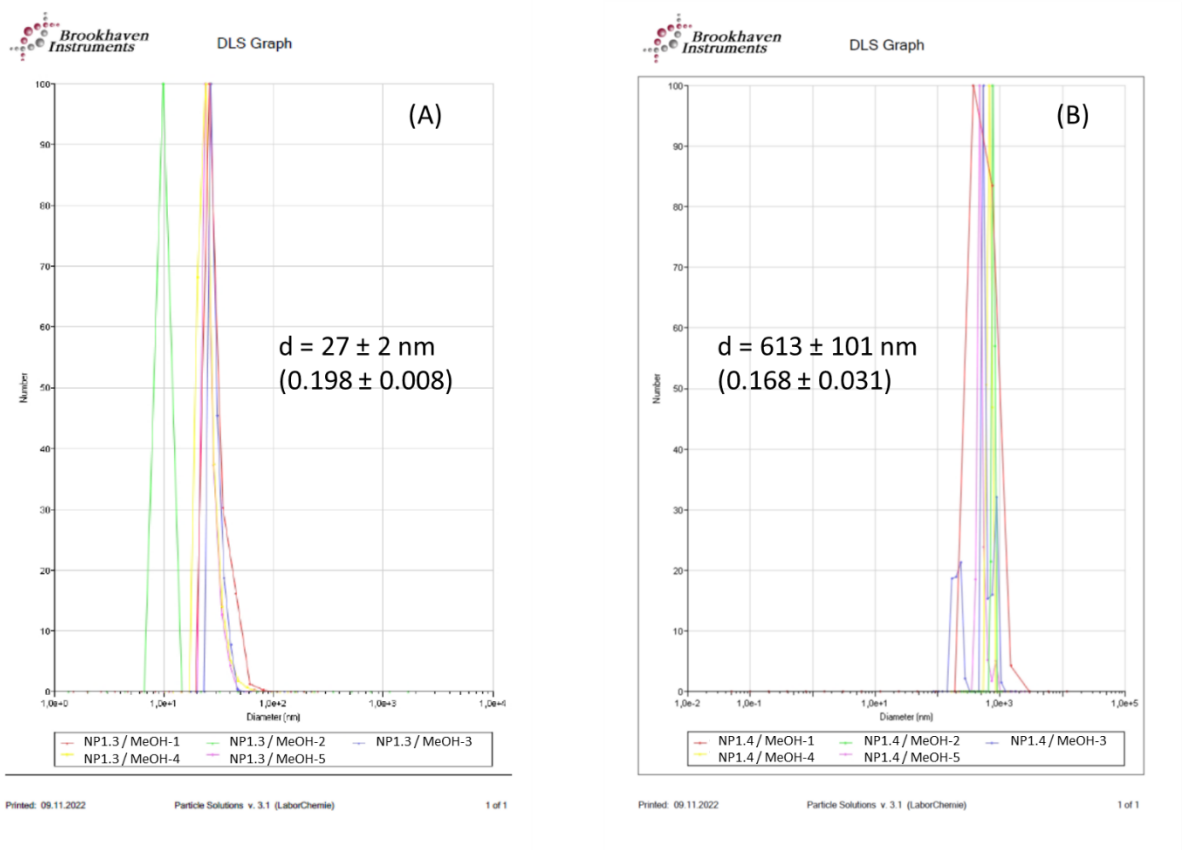


Figure S27. DLS data for NP1.3 (A) and NP1.4 (B) from five measurements in MeOH (by number distribution).

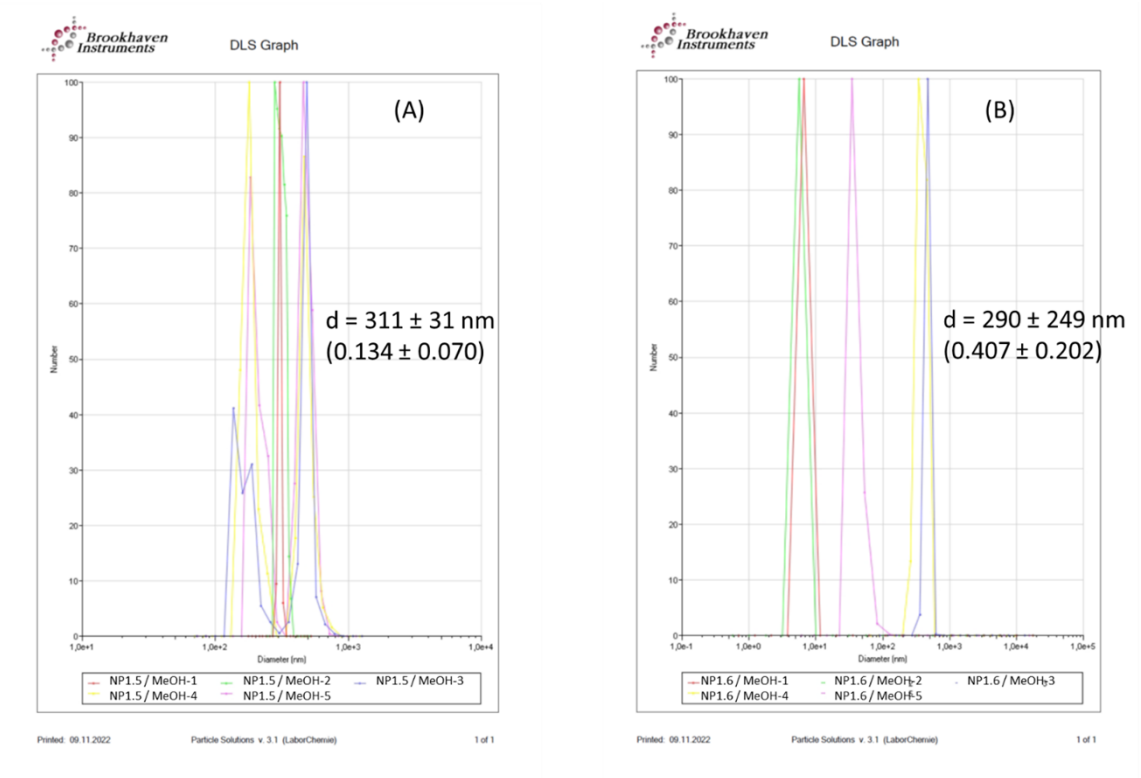


Figure S28. DLS data for NP1.5 (A) and NP1.6 (B) from five measurements in MeOH (by number distribution).

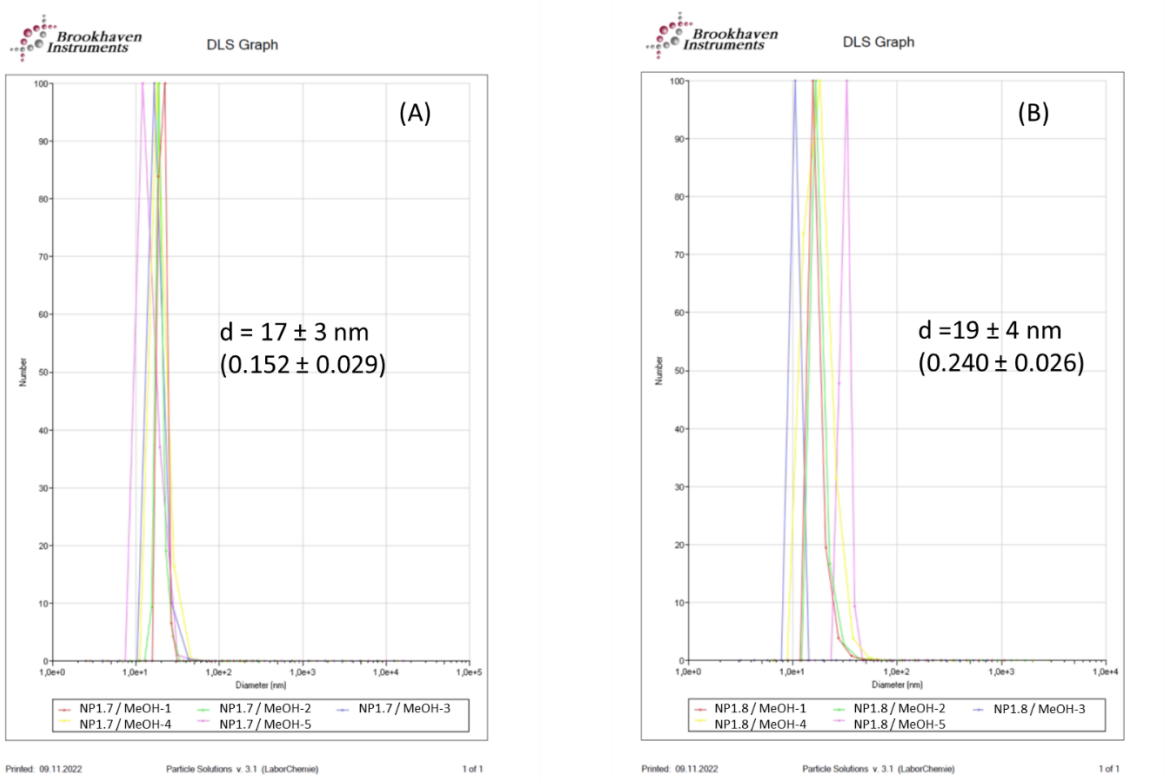


Figure S29. DLS data for NP1.7 (A) and NP1.8 (B) from five measurements in MeOH (by number distribution).

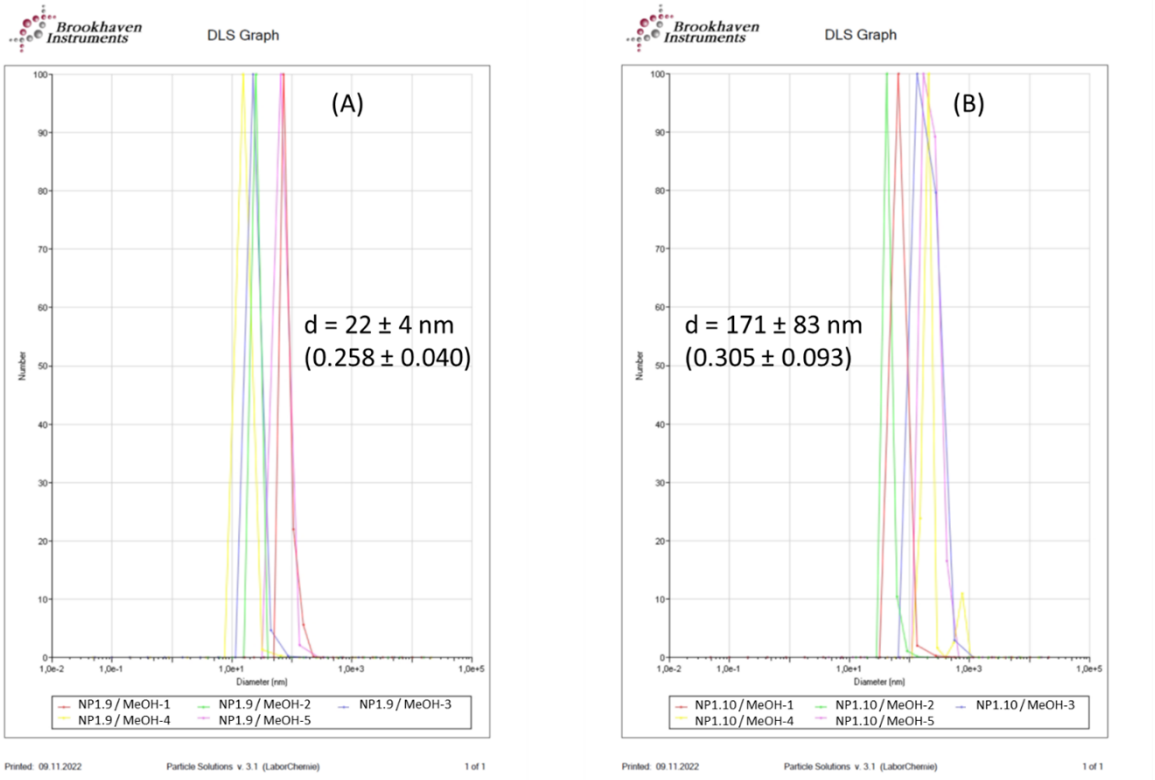


Figure S30. DLS data for NP1.9 (A) and NP1.10 (B) from five measurements in MeOH (by number distribution).

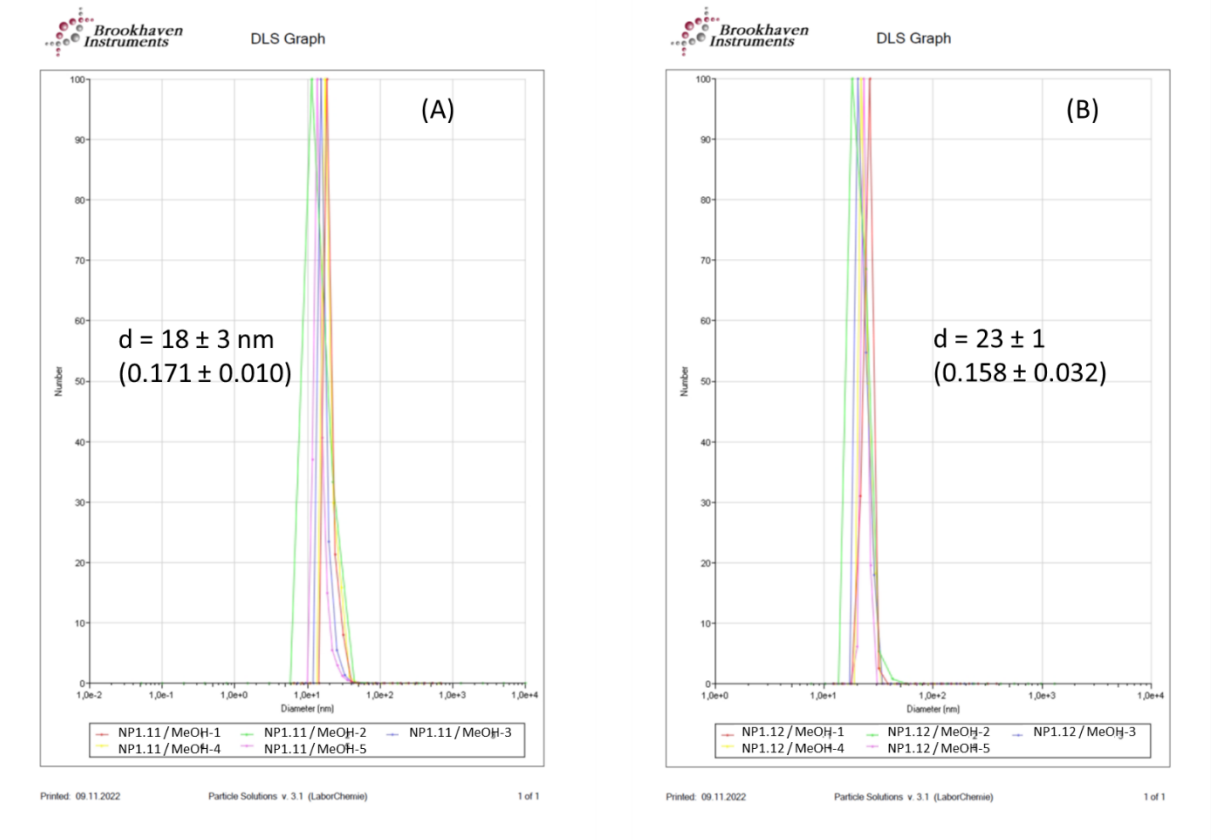


Figure S31. DLS data for NP1.11 (A) and NP1.12 (B) from five measurements in MeOH (by number distribution).

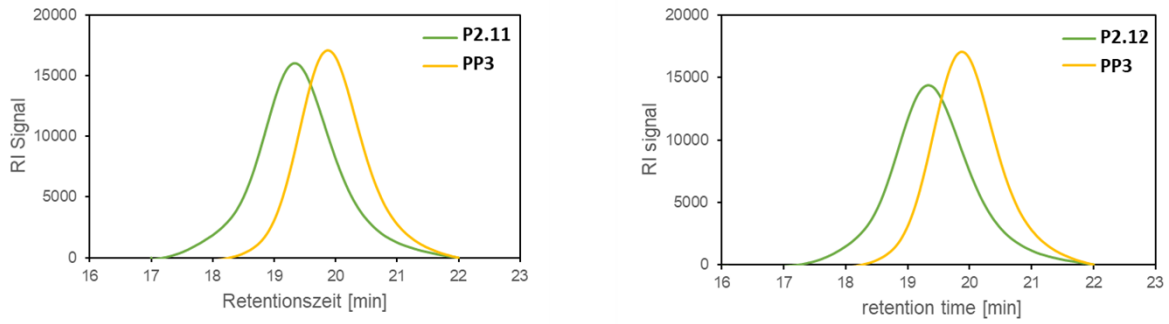


Figure S32. SEC chromatograms of the macroRAFT **PP3** and the block copolymers **P2.11** and **P2.12** (Table 1).

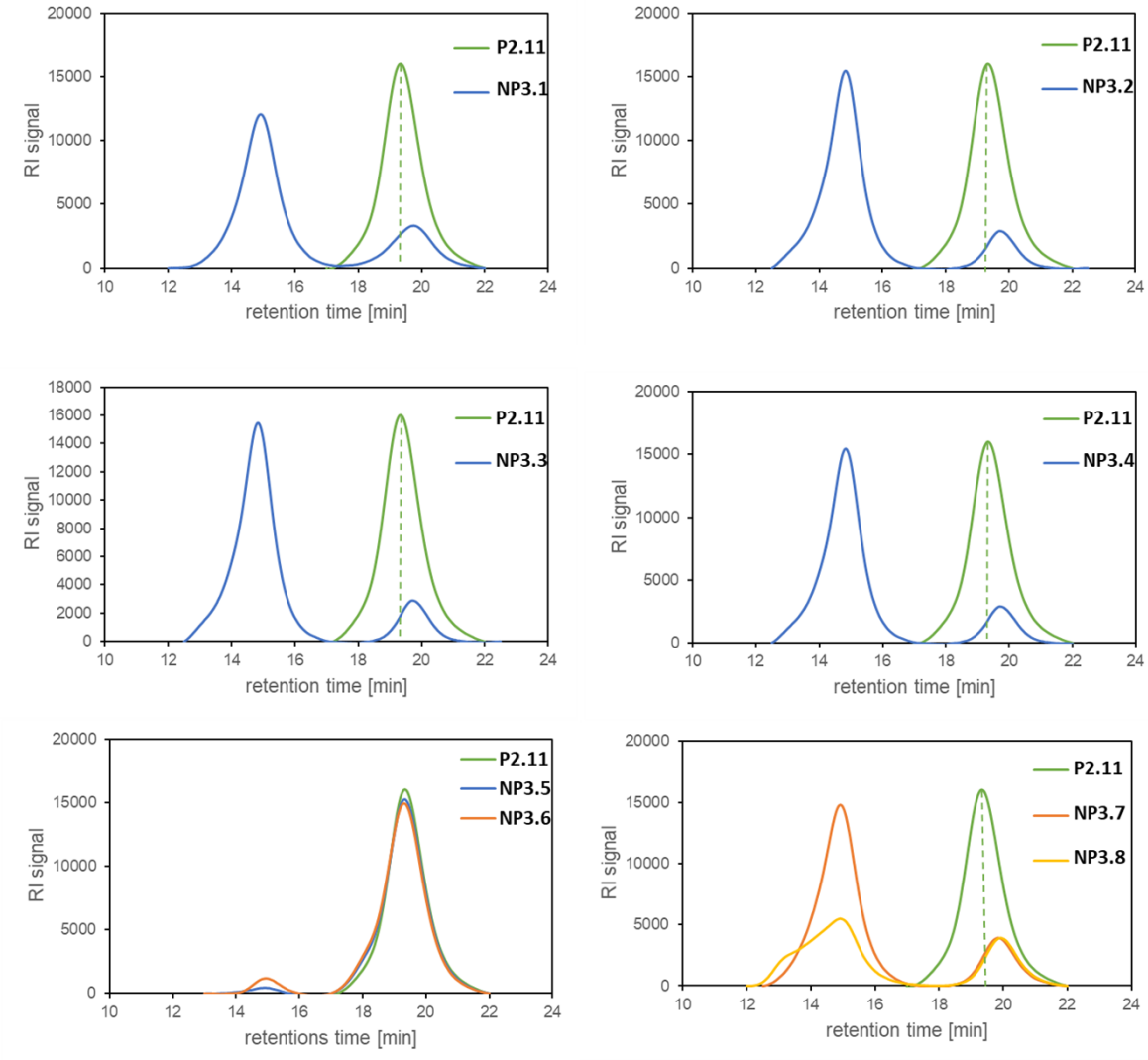


Figure S33. SEC chromatograms of the nanoparticle **NP3.1 - NP3.8** prepared from **P2.11** (Table 2). Polymer solutions of 3 mg/mL were prepared in DMF (with 5 g/L LiBr) and filtered with a syringe filter (0.2 µm). Measurements were performed at a flow rate of 1 mL/min at 35 °C.

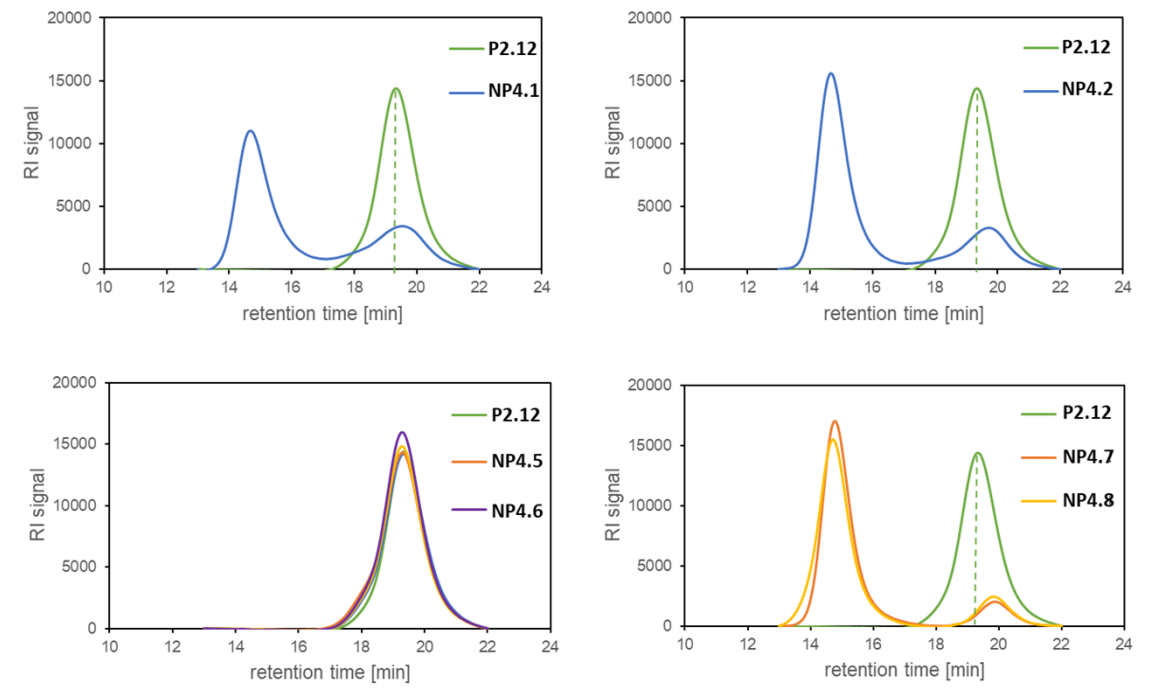


Figure S34. SEC chromatograms of the nanoparticle **NP4.1, NP4.2** and **NP4.5 – NP4.8** prepared from **P2.12** (Table 2). Polymer solutions of 3 mg/mL were prepared in DMF (with 5 g/L LiBr) and filtered with a syringe filter (0.2 µm). Measurements were performed at a flow rate of 1 mL/min at 35 °C.