

Supporting Information

Enhanced Synthesis of Multiblock Copolymers via Acid-Triggered RAFT Polymerization

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Materials and Methods

Materials

The trithiocarbamate 2-[[[(Butylsulfanyl)carbothioyl]sulfanyl] propanoic acid was synthesized via an existing protocol from N. T. Phuong in Monash University and was sent to ETH Zurich. All the other materials (methyl 2-[methyl(4-pyridinyl)carbamoithioylthio]propionate), VA-044) were purchased from Sigma Aldrich or Fischer Scientific and used as received. Acrylamide monomers (DMA and NAM) and were used without purification. Distilled water was used for all experiments. Acid solutions were prepared with H₂SO₄ (18M).

Instrumentation

¹H NMR spectra were recorded on a DPX-300 spectrometer in D₂O. Chemical shifts are given in ppm downfield from tetramethylsilane referenced to residual D₂O protons. Monomer conversions were determined via ¹H NMR spectroscopy by comparing the integrals of monomeric vinyl protons to polymer signals. Theoretical molecular weights were calculated based on the target degree of polymerization and the amount of conversion achieved. SEC analysis of polymer samples was performed using a Shimadzu modular system comprising of a CBM-20A system controller, an SIL-20A automatic injector, a 10.0 μm bead-size guard column (50 × 7.5 mm) followed by three KF-805L columns (300 × 8 mm, bead size: 10 μm, pore size maximum: 5000 Å), an SPD-20A ultraviolet detector, and an RID-20A differential refractive-index detector. The temperature of the columns was maintained at 40 °C using a CTO-20A oven. The eluent was N,N-dimethylacetamide (HPLC grade, with 0.03% w/v LiBr) and the flow rate was kept at 1 mL min⁻¹ using an LC-20AD pump. A molecular weight calibration curve was produced using commercial narrow molecular weight distribution poly(methyl methacrylate) standards with molecular weights ranging from 5000 to 1.5 × 10⁶.

RAFT Livingness equation

$$L = \frac{[CTA]_0}{[CTA]_0 + 2f[I]_{Bx} \left(1 - e^{-k_d t}\right) \left(1 - \frac{f_c}{2}\right)}$$

Equation used to calculate the livingness (L) of polymerization, where $[CTA]_0$ is the initial concentration of the chain transfer agent. k_d is the decomposition rate constant of

the VA-044 (0.0043 s^{-1}). t represents the polymerization time. The factor of 2 is because one molecule of initiator yields two primary radicals with an efficiency of $f=0.5$. This is a typical value from the literature.¹ The term $1 - (f_c/2)$ represents the number of chains produced by coupling termination events with f_c the coupling factor. $[I]_{Bx}$ is the amount of initiator present for each block synthesis, incorporating that added and what is remaining from the previous block. The method of calculation is the same as that used by Perrier and Coworkers.¹

Synthesis of PDMA DP=500 for kinetic study with CTA 1 in absence of acid (2% VA-044)

In a 15 mL vial 6.75 mg of trithiocarbamate 2- $\{[(\text{Butylsulfanyl})\text{carbothioyl}]\text{sulfanyl}\}$ propanoic acid (CTA 1, 28.5 μmol , 1 equiv.) was added. The CTA was dissolved in 1.468 mL of DMA (500 equiv.). An initiator stock solution containing 100 mg of VA-044 in 10 mL of deionized H_2O was prepared, and 18.4 μL (0.184 mg, 0.57 μmol , 0.02 equiv.) of this solution were transferred to the vial. Then 5.854 mL of water and a stirring bar were added to the vial and sealed with the septa. The solution was degassed for 15 mins, and then the polymerization was conducted at 70 °C and samples were taken periodically.

Synthesis of PDMA DP=500 for kinetic study with CTA 1 in presence of acid (2% VA-044)

In a 15 mL vial 6.75 mg of trithiocarbamate 2- $\{[(\text{Butylsulfanyl})\text{carbothioyl}]\text{sulfanyl}\}$ propanoic acid (CTA, 28.5 μmol , 1 equiv.) was added. The CTA was dissolved in 1.468 mL of DMA (500 equiv.). An initiator stock solution containing 100 mg of VA-044 in 10 mL of deionized H_2O was prepared, and 18.4 μL (0.184 mg, 0.57 μmol , 0.02 equiv.) of this solution were transferred to the vial. Then 5.854 mL of water,

15.8 uL (10 equiv., 18 M) of sulfuric acid (SA) and a stirring bar were added to the vial and sealed with the septa. The solution was degassed for 15 mins, and then the polymerization was conducted at 70 °C and samples were taken periodically.

Synthesis of PDMA DP=500 for kinetic study with CTA 1 in the absence of acid (8% VA-044)

In a 15 mL vial 7.7 mg of trithiocarbamate 2-[[[(Butylsulfanyl)carbothioyl]sulfanyl]propanoic acid (CTA, 28.5 μmol, 1 equiv.) was added. The CTA was dissolved in 1.468 mL of DMA (500 equiv.). An initiator stock solution containing 100 mg of VA-044 in 10 mL of deionized H₂O was prepared, and 73.6 uL (0.736 mg, 2.16 μmol, 0.08 equiv.) of this solution were transferred to the vial. The solution was degassed for 15 mins, and then the polymerization was conducted at 70 °C and samples were taken periodically.

Synthesis of PDMA DP=500 for kinetic study with CTA 2 in presence of acid

In a 15 mL vial 7.7 mg of methyl 2-[methyl(4 -pyridinyl)carbamoithioylthio]propionate (CTA, 28.5 μmol, 1 equiv.) was added. The CTA was dissolved in 1.468 mL of DMA (500 equiv.). An initiator stock solution containing 100 mg of VA-044 in 10 mL of deionized H₂O was prepared, and 18.4 uL (0.184 mg, 0.57 μmol, 0.02 equiv.) of this solution were transferred to the vial. Then 5.854 mL of water, 15.8 uL (10 equiv., 18 M) of sulfuric acid (SA) and a stirring bar were added to the vial and sealed with the septa. The solution was degassed for 15', and then the polymerization was conducted at 70°C and samples were taken periodically.

Synthesis of pentablock copolymer (DP=100) via conventional RAFT

In a 15 mL vial 6.8 mg of 2-(((Butylsulfanyl)carbothioyl)sulfanyl)propanoic acid (CTA, 28.5 μmol, 1 equiv.) was added. The CTA was dissolved in 0.293 mL of DMA

(100 equiv.). An initiator stock solution containing 100 mg of VA-044 in 10 mL of deionized H₂O was prepared, and 24.9 uL (0.027 equiv.) of this solution were transferred to the vial. Then 1.151 mL of water, and a stirring bar were added to the vial and sealed with the septa. The solution was degassed for 15 mins, and then the polymerization was conducted at 70 °C for 75 minutes to reach a high conversion (97%). In a separate vial, 0.358 ml of NAM (0.402 g, 2.85 mmol, 100 equiv., 20% solution v/v and 16.6 μL of initiator solution (0.166 mg, 0.51 μmol, 0.018 equiv.) were mixed and degassed together for 15 minutes prior to addition to the polymerization mixture via a nitrogen purged syringe. Polymerization was again conducted for 65 mins, yielding a diblock copolymer with high conversion (>99%). The same procedure was followed for the three additional blocks.

Synthesis of pentablock copolymer (DP=100) via acid-triggered RAFT

In a 15 mL vial 7.7 mg of methyl 2-[methyl(4-pyridinyl)carbamothioylthio]propionate (CTA, 28.5 μmol, 1 equiv.) was added. The CTA was dissolved in 0.293 mL of DMA (100 equiv.). An initiator stock solution containing 100 mg of VA-044 in 10 mL of deionized H₂O was prepared, and 12.3 uL (0.0133 equiv.) of this solution were transferred to the vial. Then 1.159 mL of water, 4.75 uL (3 equiv., 18 M) of sulfuric acid (SA) and a stirring bar were added to the vial and sealed with the septa. The solution was degassed for 15 mins, and then the polymerization was conducted at 70 °C for 120 minutes to reach a high conversion (97%). In a separate vial, 0.358 ml of NAM (0.402 g, 2.85 mmol, 100 equiv., 20% solution v/v, 3.17 uL (18 M) 6.2 μL of initiator solution (0.062 mg, 0.19 μmol, 0.0067 equiv.) were mixed and degassed together for 15 minutes prior to addition to the polymerization mixture via a nitrogen purged syringe. Polymerization was again conducted for 65 mins, yielding a diblock

copolymer with high conversion (>99%). The same procedure was followed for the three additional blocks.

Synthesis of pentablock copolymer (DP=100) via acid-triggered RAFT (without any VA-044)

In a 5 mL vial 7.7 mg of methyl 2-[methyl(4-pyridinyl)carbamothioylthio]propionate (CTA, 28.5 μmol , 1 equiv.) was added. The CTA was dissolved in 0.293 mL of DMA (100 equiv.). Then 0.293 mL of water, 1.2 μL (18 M) of sulfuric acid (SA) and a stirring bar were added to the vial and sealed with the septa. The solution was degassed for 15 mins, and then the polymerization was conducted at 70 °C for 20 hours to reach a high conversion (94%). In a separate vial, 0.358 ml of NAM (0.402 g, 2.85 mmol, 100 equiv., 42% solution v/v and 0.5 μL (18 M) were mixed and degassed together for 15 minutes prior to addition to the polymerization mixture via a nitrogen purged syringe. Polymerization was again conducted for 20 hours, yielding a diblock copolymer with high conversion (>99%). The same procedure was followed for the three additional blocks.

Synthesis of pentablock copolymer (DP=200) via acid-triggered RAFT

In a 15 mL vial 7.7 mg of methyl 2-[methyl(4-pyridinyl)carbamothioylthio]propionate (CTA, 28.5 μmol , 1 equiv.) was added. The CTA was dissolved in 0.587 mL of DMA (200 equiv.). An initiator stock solution containing 100 mg of VA-044 in 10 mL of deionized H₂O was prepared, and 8.29 μL (0.0070 equiv.) of this solution were transferred to the vial. Then 2.34 mL of water, 4.75 μL (3 equiv., 18 M) of sulfuric acid (SA) and a stirring bar were added to the vial and sealed with the septa. The solution was degassed for 15 min, and then the polymerization was conducted at 70°C for 75 minutes to reach a high conversion (97%). In a separate vial, 0.717 ml of NAM (0.804

g, 5.7 mmol, 200 equiv., 20% solution v/v and 3.04 μL of initiator solution (0.09 μmol , 0.0033 equiv.) were mixed and degassed together for 15 minutes prior to addition to the polymerization mixture via a nitrogen purged syringe. Polymerization was again conducted for 65 min, yielding a diblock copolymer with high conversion (>99%). The same procedure was followed for the triblock, tetrablock, and pentablock respectively.

Synthesis of pentablock copolymer (DP=500) via acid-triggered RAFT

In a 15 mL vial 3.2mg of methyl 2-[methyl(4-pyridinyl)carbamothioylthio]propionate (CTA, 36.2 μmol , 1 equiv.) was added. The CTA was dissolved in 0.610 mL of DMA (500 equiv.). An initiator stock solution containing 100 mg of VA-044 in 10 mL of deionized H_2O was prepared, and 7.73 μL (0.0202 equiv.) of this solution were transferred to the vial. Then 2.431 mL of water, 6.57 μL (10 equiv., 18 M) of sulfuric acid (SA) and a stirring bar were added to the vial and sealed with the septa. The solution was degassed for 15', and then the polymerization was conducted at 70°C for 90 minutes to reach a high conversion (97%). In a separate vial, 0.745 ml of NAM (0.836 g, 5.9 mmol, 500 equiv., 20% solution v/v and 4.59 μL of initiator solution (0.046 mg, 0.14 μmol , 0.0120 equiv.) were mixed and degassed together for 15 minutes prior to addition to the polymerization mixture via a nitrogen purged syringe. Polymerization was again conducted for 90', yielding a diblock copolymer. This process was repeated for all subsequent blocks.

Synthesis of icosablock copolymer (B1 DP=30, B2-B20 DP=6)

In a 5 mL vial 31.2 mg of methyl 2-[methyl(4-pyridinyl)carbamothioylthio]propionate (CTA, 36.2 μmol , 1 equiv.) was added. The CTA was dissolved in 0.436 mL of NAM (30 equiv.). An initiator stock solution containing 100 mg of VA-044 in 10 mL of deionized H_2O was prepared, and 11.19 μL (0.0030 equiv.) of this solution were

transferred to the vial. Then 2.457 mL of water, 6.40 μL (1 equiv., 18 M) of sulfuric acid (SA) and a stirring bar were added to the vial and sealed with the septa. The solution was degassed for 15 mins under argon, and then the polymerization was conducted at 70 °C for 50 minutes to reach a high conversion (99%). In a separate vial, 0.0714 ml of DMA (68.7 mg, 0.69 mmol, 6 equiv., 20% solution v/v and 6.34 μL of initiator solution (0.063 mg, 0.20 μmol , 0.0017 equiv.) were mixed and degassed together for 15 minutes prior to addition to the polymerization mixture via a nitrogen purged syringe. Polymerization was again conducted for 50 mins, yielding a diblock copolymer. This process was repeated for all subsequent blocks. After block 7, the reaction was stopped, and half of the quantity was removed from the vial. The solution remaining in the vial was again degassed for 15'. On parallel in a separate vial the aliquot containing block 8 was also degassed, and with a degassed needle the aliquot is transferred to the reaction vial. The polymerization is conducted at 70°C to reach a high conversion (97%). The same procedure was followed for all the subsequent blocks until an icosablock was synthesized.

Synthesis of pentablock copolymer with methacrylate, acrylate, and acrylamide via conventional RAFT

In a 5 mL vial 7.5 mg of 4-(((2-Carboxyethyl)thio)carbonothioyl)thio)-4-cyanopentanoic acid (CTA, 24.4 μmol , 1 equiv.) and 0.52 mL of glycerol monomethacrylate (11.2 % v/v, 15 equiv.) was added. An initiator stock solution containing 100 mg of VA-044 in 10 mL of deionized H_2O was prepared, and 17.4 μL (0.022 equiv.) of this solution was transferred to the vial. Then a stirring bar was added to the vial and sealed with the septa. The solution was degassed for 15 mins, and then the polymerization was conducted at 70 °C for 120 minutes to reach a high conversion (98%). In a separate vial, 0.16 ml of PEGA₄₈₀ (0.17 g, 0.37 mmol, 15 equiv., 20%

solution v/v and 23.7 μL of initiator solution (0.73 μmol , 0.030 equiv.) were mixed and degassed together for 15 minutes prior to addition to the polymerization mixture via a nitrogen purged syringe. Polymerization was again conducted for 120 mins, yielding a diblock copolymer with high conversion (>99%). The same procedure was followed for the three additional blocks.

Synthesis of pentablock copolymer with methacrylate, acrylate, and acrylamide via acid-triggered RAFT

In a 5 mL vial 7.5 mg of 4-(((2-Carboxyethyl)thio)carbonothioyl)thio)-4-cyanopentanoic acid (CTA, 24.4 μmol , 1 equiv.) and 0.52 mL of glycerol monomethacrylate (11.2 % v/v, 15 equiv.) was added. An initiator stock solution containing 100 mg of VA-044 in 10 mL of deionized H_2O was prepared, and 11.8 μL (0.37 mmol, 0.015 equiv.) of this solution and 0.7 μL of H_2SO_4 (18 M) was transferred to the vial. Then a stirring bar was added to the vial and sealed with the septa. The solution was degassed for 15 mins, and then the polymerization was conducted at 70 $^\circ\text{C}$ for 120 minutes to reach a high conversion (>99%). In a separate vial, 0.16 ml of PEGA₄₈₀ (0.17 g, 0.37 mmol, 15 equiv., 20% solution v/v, 14.2 μL of initiator solution (0.44 μmol , 0.018 equiv.) and 1.5 μL of H_2SO_4 (18 M) were mixed and degassed together for 15 minutes prior to addition to the polymerization mixture via a nitrogen purged syringe. Polymerization was again conducted for 120 mins, yielding a diblock copolymer with high conversion (97%). The same procedure was followed for the three additional blocks.

Data corresponding to Figure 2

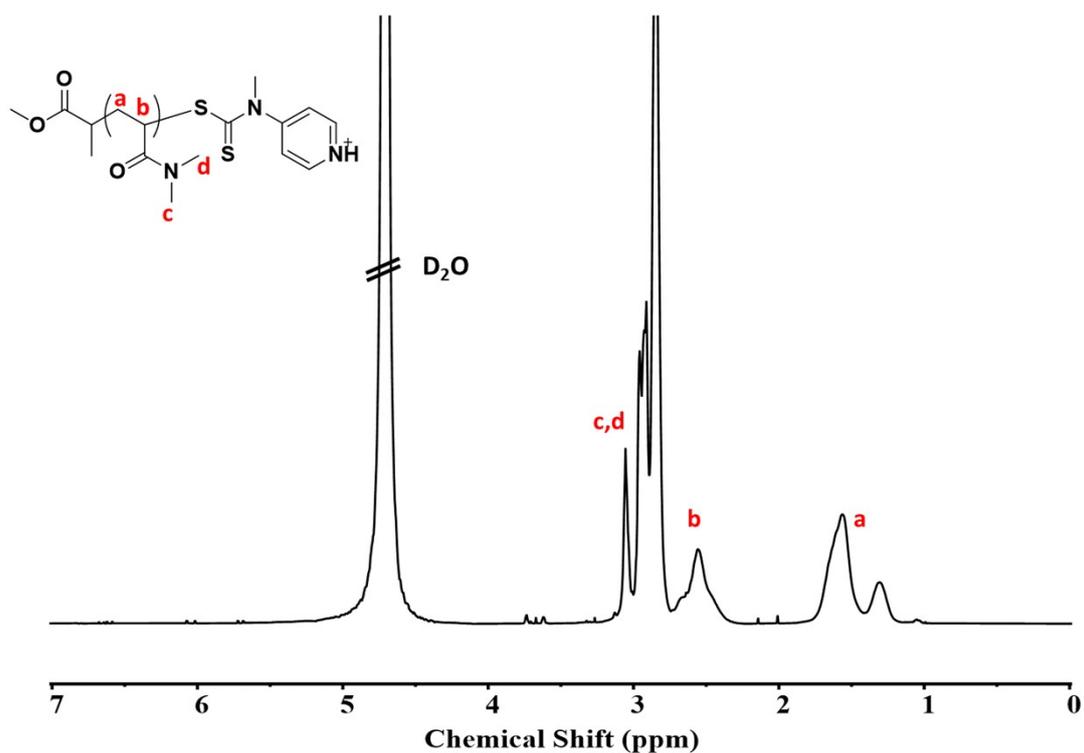


Figure S1. A representative ¹H NMR spectra of PDMA homopolymer synthesized by RAFT polymerization

Table S1. Experimental conditions and characterization data for the kinetic study of PDMA for DP=500. Data corresponds to Figure 2.

Entry	CTA	CTA (mg)	CTA (10 ⁻⁵ mol)	DP	M	Monomer (10 ⁻³ mol)	Monomer (mL)	[VA-044]:[CTA]	VA-044 (10 ⁻⁷ mol)	Initiator (ul)	M%	H ₂ SO ₄ (uL)	H ₂ O (mL)	V _{tot} (mL)
1	CTA 1	6.8	2.85	500	DMA	14.2	1.468	0.02	5.7	18.4	0.2	-	5.85	7.34

2	CTA 1	6.8	2.85	500	DMA	14.2	1.468	0.02	5.7	18.4	0.2	15.8	5.85	7.34
3	CTA 1	6.8	2.85	500	DMA	14.2	1.468	0.08	22.8	73.6	0.2	-	5.85	7.34
4	CTA 2	7.7	2.85	500	DMA	14.2	1.468	0.02	5.7	18.4	0.2	15.8	5.85	7.34

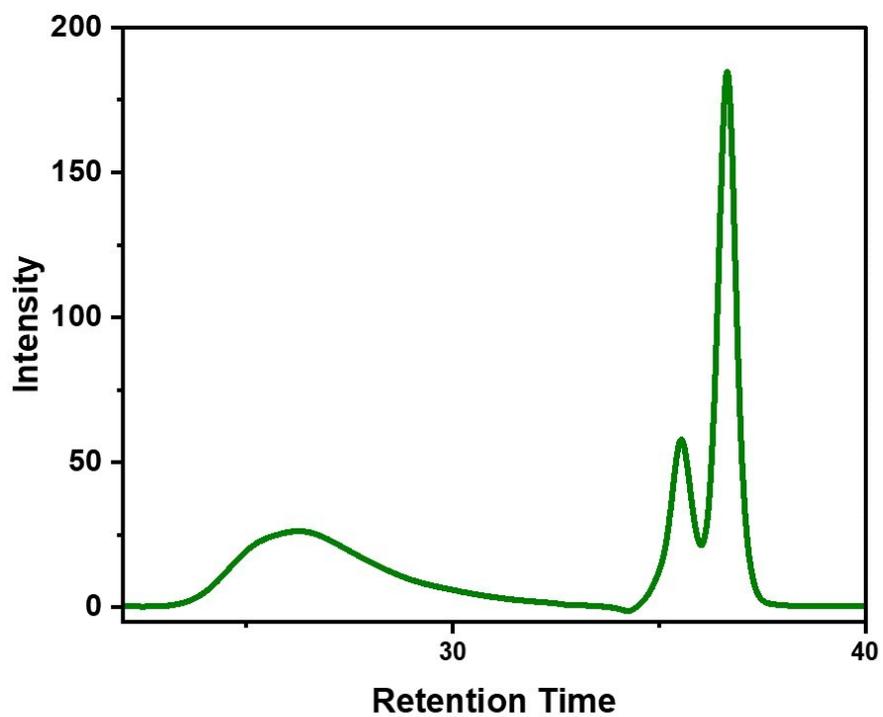


Figure S2. UV-trace of PDMA kinetic with CTA 1 and 2% VA-044 at final conversion (30%). The peak at 35.5 min represents the unreacted monomer and the peak at 36.6 the unreacted CTA.

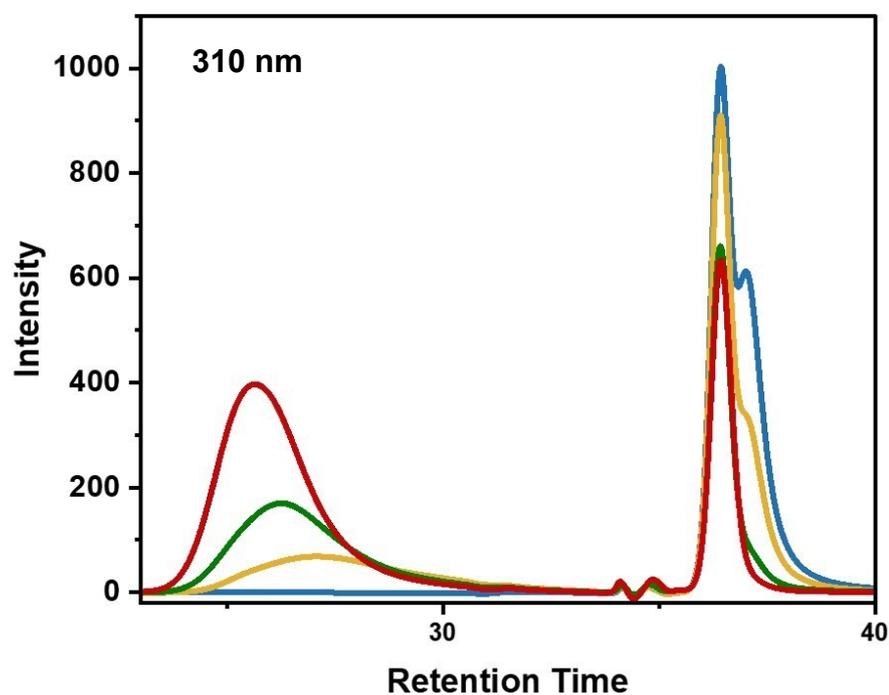


Figure S3. UV-trace of PDMA kinetic with CTA 1, 8% VA-044 and no acid. The blue trace represents t_0 . The dark yellow trace at 16% there is unreacted CTA. At 42% conversion (green trace) there is still unreacted CTA. At 64% conversion (red trace) the CTA has been fully consumed. Full CTA consumption is achieved between 42% and 64% conversion.

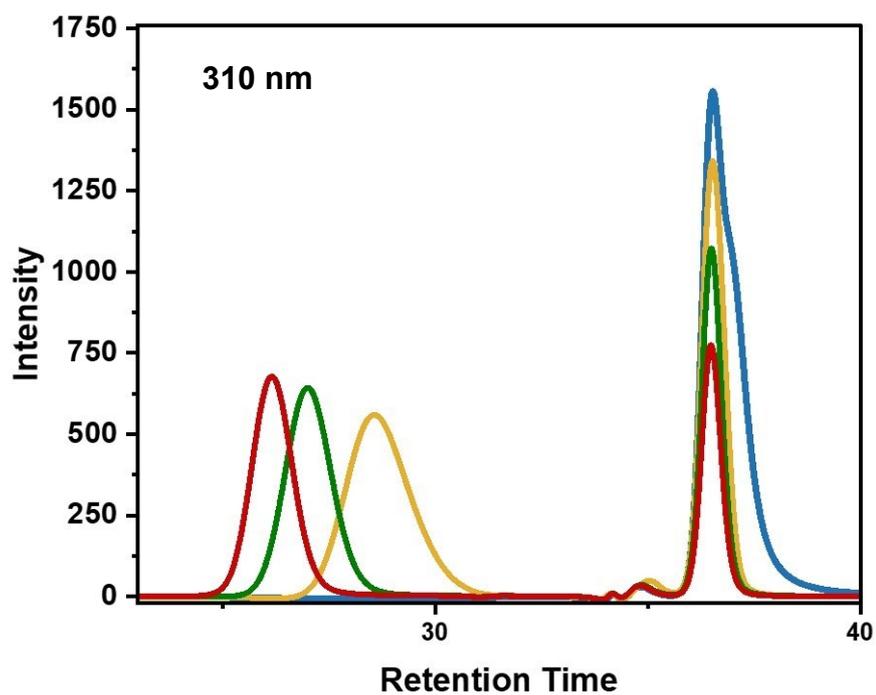


Figure S4. UV-trace of PDMA kinetic with CTA 1, 2% VA-044 and 10 eq. of acid. The blue trace represents t_0 . The dark yellow trace at 14% conversion shows the full consumption of the CTA.

Data corresponding to Figure 3

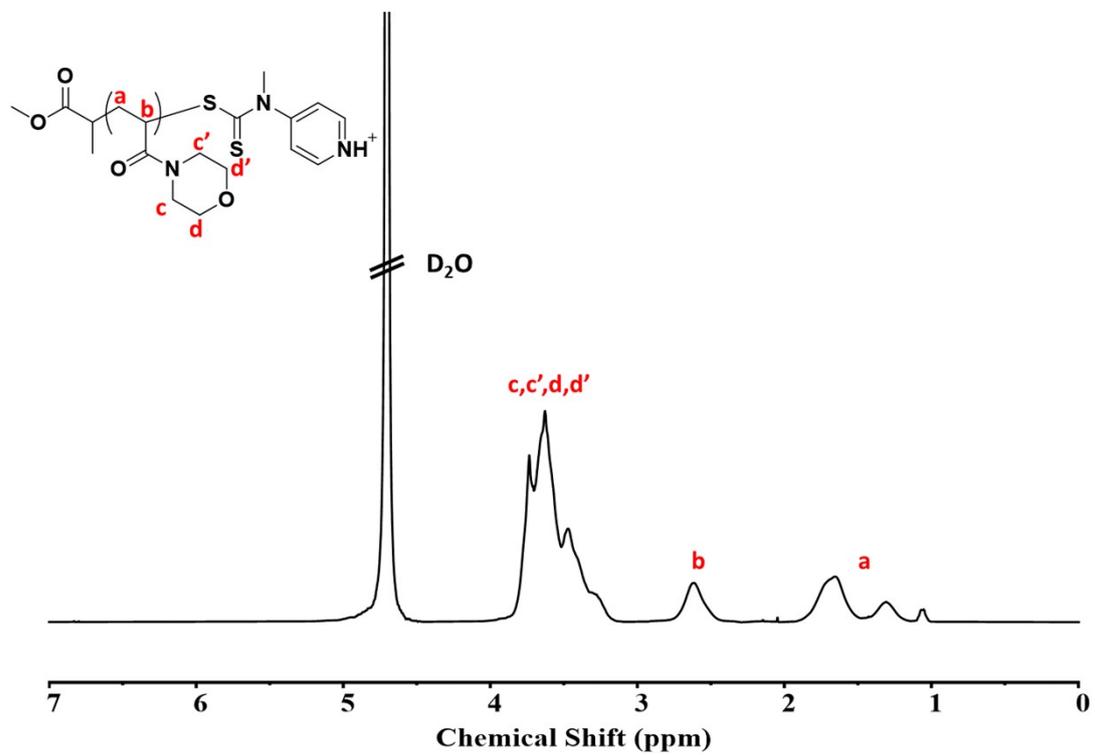


Figure S5. A representative ¹H NMR spectra of PNAM homopolymer synthesized by RAFT polymerization.

Table S2. Experimental conditions and characterization data for the synthesis of P(DMA-b-NAM-b-DMA-b- NAM-b -DMA-b-NAM-b-DMA-b-NAM-b-DMA-b- NAM) pentablock copolymer with DP=100.^[a] Data corresponds to Figure 3a-3c.

No. block	CTA 1 (mg)	CTA (10 ⁻⁵ mol)	DP	M	Monomer (10 ⁻³ mol)	Monomer (mL)	[VA-044]:[CTA] ^[b]	VA-044 (10 ⁻⁷ mol)	I _{added} (ul) ^[c]	M%	H ₂ SO ₄ (uL)	H ₂ O (mL)	Vtot (mL)	Irem (10 ⁻⁸ mol)	Itot (10 ⁻⁷ mol) ^[d]	% Conv. ^[e]	\bar{D}	$M_n^{(Theo.)}$ (g mol ⁻¹) ^[f]	$M_n^{(SEC)}$	%L Block	%L Total
1	6.8	2.85	100	DMA	2.85	0.293	0.027	7.7	24.9	0.2	-	1.151	1.467		7.7	94	1.09	9600	12300	97.5	97.5
2	-	-	100	NAM	2.85	0.358	0.018	5.1	16.6	0.2	-	1.419	1.792	3.5	5.5	97	1.13	23200	27100	98.2	95.7
3	-	-	100	DMA	2.85	0.293	0.022	6.3	20.3	0.2	-	1.155	1.467	2.5	6.5	96	1.20	32800	38900	97.8	93.6
4	-	-	100	NAM	2.85	0.358	0.020	5.7	18.4	0.2	-	1.417	1.792	3.0	6.0	97	1.28	46500	22900	98.0	91.7
5	-	-	100	DMA	2.85	0.293	0.023	6.6	21.2	0.2	-	1.154	1.467	2.7	2.7	93	1.38	55700	62300	97.7	89.6

[a] All polymerizations were performed in Water at 70 C with 120 reaction time per block. The volume ratio of solvent to monomer was maintained at 0.80:0.20. [b] [CTA] refers to the initial equivalents of 2-((Butylsulfanyl)carbothioyl)sulfanyl)propanoic acid and subsequently the equivalents of macroCTA derived from this CTA. No additional CTA was added during the subsequent block additions. [c] Initiator solution of 100 mg VA-044 in 10 mL H₂O (0.0309 M). [d] Represents the total amount of VA-044 at time t0 considering the moles of VA-044 added (I_{added}) + the moles of VA-044 remaining (I_{rem}) from the previous block after 2h. I_{rem} = I_{total} - 2fe^{-kd_{th}t} (1-fc/2)^[1]. [e] Conversion was calculated by ¹H NMR. [f] $M_n^{(theory)} = ([Monomer]_0/[CTA]_0) \cdot p \cdot M_{monomer} + M_{CTA}$, where [Monomer]₀/[CTA]₀ is the ratio of monomer to CTA at time zero, p is the conversion of polymerization and M_{monomer} and M_{CTA} are the molecular weights of the monomer and the CTA.

Table S3. Experimental conditions and characterization data for the synthesis of P(DMA-b-NAM-b-DMA-b- NAM-b -DMA-b-NAM-b-DMA-b-NAM-b-DMA-b- NAM) pentablock copolymer with DP=100.^[a] Data corresponds to Figure3d-3c.

No. block	CTA 2 (mg)	CTA (10 ⁻⁵ mol)	DP	M	Monomer (10 ⁻³ mol)	Monomer (mL)	[VA-044]:[CTA] ^[b]	VA-044 (10 ⁻⁷ mol)	I _{added} (ul) ^[c]	M%	H ₂ SO ₄ (uL)	H ₂ O (mL)	Vtot (mL)	Irem (10 ⁻⁸ mol)	Itot (10 ⁻⁷ mol) ^[d]	% Conv. ^[e]	\bar{D}	$M_n^{(Theo.)}$ (g mol ⁻¹) ^[f]	$M_n^{(SEC)}$	%L Block	%L Total
1	7.7	2.85	100	DMA	2.85	0.293	0.0133	3.8	12.3	0.2	4.75	1.159	1.467		3.8	97	1.16	9900	10400	99.0	99.0
2	-	-	100	NAM	2.85	0.358	0.0067	1.9	6.2	0.2	3.17	1.427	1.792	6.2	2.5	99	1.16	23900	24200	99.3	98.3
3	-	-	100	DMA	2.85	0.293	0.0100	4.3	13.8	0.2	3.17	1.160	1.467	4.2	4.7	97	1.14	33500	36600	98.7	97.0
4	-	-	100	NAM	2.85	0.358	0.0093	2.6	8.5	0.2	3.17	1.425	1.792	7.7	3.4	98	1.16	47300	48200	99.0	96.1
5	-	-	100	DMA	2.85	0.293	0.0120	3.5	11.0	0.2	3.17	1.163	1.467	5.6	4.0	98	1.17	57000	60300	98.9	95.0

[a] All polymerizations were performed in Water at 70 C with 120 reaction time per block. The volume ratio of solvent to monomer was maintained at 0.80:0.20. [b] [CTA] refers to the initial equivalents of methyl 2-[methyl(4-pyridinyl)carbamothioylthio]propionate and subsequently the equivalents of macroCTA derived from this CTA. No additional CTA was added during the subsequent block additions. [c] Initiator solution of 100 mg VA-044 in 10 mL H₂O (0.0309 M). [d] Represents the total amount of VA-044 at time t0 considering the moles of VA-044 added (I_{added}) + the moles of VA-044 remaining (I_{rem}) from the previous block after 2h. I_{rem} = I_{total} - 2fe^{-kd_{th}t} (1-fc/2)^[1]. [e] Conversion was calculated by ¹H NMR. [f] $M_n^{(theory)} = ([Monomer]_0/[CTA]_0) \cdot p \cdot M_{monomer} + M_{CTA}$, where [Monomer]₀/[CTA]₀ is the ratio of monomer to CTA at time zero, p is the conversion of polymerization and M_{monomer} and M_{CTA} are the molecular weights of the monomer and the CTA.

Table S4. Experimental conditions and characterization data for the synthesis of P(DMA-b-NAM-b-DMA-b- NAM-b -DMA-b-NAM-b-DMA-b-NAM-b-DMA-b- NAM) pentablock copolymer with DP=100.^[a] Data corresponds to Figure3d-3c.

No. block	CTA 2 (mg)	CTA (10 ⁻⁵ mol)	DP	M	Monomer (10 ⁻³ mol)	Monomer (mL)	[VA-044]:[CTA] ^[b]	VA-044 (10 ⁻⁷ mol)	I _{added} (μl) ^[c]	M%	H ₂ SO ₄ (μL)	H ₂ O (mL)	Vtot (mL)	% Conv. ^[e]	\bar{D}	$M_n^{(Theo.)}$ (g mol ⁻¹) ^[f]	$M_n^{(SEC)}$	Time (h)
1	7.7	2.85	100	DMA	2.85	0.293	-	-	-	0.50	1.2	0.29	0.58	94	1.25	9600	8600	20
2	-	-	100	NAM	2.85	0.358	-	-	-	0.42	0.5	0.50	0.86	>99.9	1.23	23700	22600	20
3	-	-	100	DMA	2.85	0.293	-	-	-	0.33	0.3	0.60	0.89	>99.9	1.19	33600	39600	22
4	-	-	100	NAM	2.85	0.358	-	-	-	0.32	0.2	0.75	1.11	>99.9	1.17	47700	60400	20
5	-	-	100	DMA	2.85	0.293	-	-	-	0.31	0.7	0.65	0.94	97	1.23	57300	75300	24

[a] All polymerizations were performed in Water at 70 °C with 120 reaction time per block. The volume ratio of solvent to monomer was maintained at 0.80:0.20. [b] [CTA] refers to the initial equivalents of methyl 2-[methyl(4-pyridinyl)carbamothioylthio]propionate and subsequently the equivalents of macroCTA derived from this CTA. No additional CTA was added during the subsequent block additions. [c] Initiator solution of 100 mg VA-044 in 10 mL H₂O (0.0309 M). [d] Represents the total amount of VA-044 at time t0 considering the moles of VA-044 added (I_{added}) + the moles of VA-044 remaining (I_{rem}) from the previous block after 2h. I_{rem} = I_{total} - 2fe^{-kdIt} (1-fc/2)^[1]. [e] Conversion was calculated by ¹H NMR. [f] $M_n^{(theory)} = ([Monomer]_0/[CTA]_0) \cdot p \cdot M_{monomer} + M_{CTA}$, where [Monomer]₀/[CTA]₀ is the ratio of monomer to CTA at time zero, p is the conversion of polymerization and M_{monomer} and M_{CTA} are the molecular weights of the monomer and the CTA.

Data corresponding to Figure 4

Table S5. Experimental conditions and characterization data for the synthesis of P(DMA-b-NAM-b-DMA-b- NAM-b -DMA) pentablock copolymer with DP=200.^[a] Data corresponds to Figure 2a-2c.

No. block	CTA 2 (mg)	CTA (10 ⁻⁵ mol)	DP	M	Monomer (10 ⁻³ mol)	Monomer (mL)	[VA-044]:[CTA] _[b]	VA-044 (10 ⁻⁷ mol)	I _{added} (ul) ^[c]	M%	H ₂ SO ₄ (uL)	H ₂ O (mL)	Vtot (mL)	Irem (10 ⁻⁸ mol)	Itot (10 ⁻⁷ mol) ^[d]	% Conv. _[e]	Đ	M _n ^(Theo.) (g mol ⁻¹) _[f]	M _n ^(SEC)	%L Block	%L Total
1	7.7	2.8	200	DMA	5.7	0.58694	0.0070	1.96	8.29	0.2	4.75	2.34	2.93		2.6	97	1.15	19500	20900	99.4	99.4
2	-	-	200	NAM	5.7	0.71666	0.0033	0.94	3.04	0.2	3.17	2.86	3.58	3.7	1.3	99	1.18	47500	45500	99.6	99.0
3	-	-	200	DMA	5.7	0.58694	0.0054	1.50	4.97	0.2	3.17	2.33	2.93	1.9	1.7	98	1.17	66900	68300	99.5	98.6
4	-	-	200	NAM	5.7	0.71666	0.0158	4.50	14.55	0.2	3.17	2.84	3.58	2.5	4.7	>99.9	1.19	95100	93100	98.6	97.2
5	-	-	200	DMA	5.7	0.58694	0.0248	7.10	22.83	0.2	3.17	2.32	3.58	6.9	7.7	98	1.22	114500	116600	97.8	95.0

[a] All polymerizations were performed in Water at 70 °C with 120 reaction time per block. The volume ratio of solvent to monomer was maintained at 0.80:0.20. [b] [CTA] refers to the initial equivalents of methyl 2-[methyl(4-pyridinyl)carbamothioylthio]propionate and subsequently the equivalents of macroCTA derived from this CTA. No additional CTA was added during the subsequent block additions. [c] Initiator solution of 100 mg VA-044 in 10 mL H₂O (0.0309 M). [d] Represents the total amount of VA-044 at time t₀ considering the moles of VA-044 added (I_{added}) + the moles of VA-044 remaining (I_{rem}) from the previous block after 2h. I_{rem} = I_{total} - 2fe^{-kd_{th}t} (1-fc/2)^[1]. [e] Conversion was calculated by ¹H NMR. [f] M_n(theory) = ([Monomer]₀/[CTA]₀)^p Mmonomer + M_{CTA}, where [Monomer]₀/[CTA]₀ is the ratio of monomer to CTA at time zero, p is the conversion of polymerization and Mmonomer and M_{CTA} are the molecular weights of the monomer and the CTA.

Table S6. Experimental conditions and characterization data for the synthesis of P(DMA-b-NAM-b-DMA-b- NAM-b -DMA) pentablock copolymer with DP=500.^[a] Data corresponds to Figure 2c-2d.

No. block	CTA 2 (mg)	CTA (10 ⁻⁵ mol)	DP	M	Monomer (10 ⁻³ mol)	Monomer (mL)	[VA-044]:[CTA] _[b]	VA-044 (10 ⁻⁷ mol)	I _{added} (ul) ^[c]	M%	H ₂ SO ₄ (uL)	H ₂ O (mL)	Vtot (mL)	Irem (10 ⁻⁸ mol)	Itot (10 ⁻⁷ mol) ^[d]	% Conv. _[e]	Đ	M _n ^(Theo.) (g mol ⁻¹) _[f]	M _n ^(SEC)	%L Block	%L Total
1	3.2	1.18	500	DMA	5.9	0.60981	0.0202	2.4	7.73	0.2	6.58	2.431	3.049		2.40	97	1.16	48300	54900	98.1	98.1
2	-	-	500	NAM	5.9	0.74458	0.0120	1.4	4.59	0.2	6.58	2.974	3.723	1.10	1.53	98	1.19	117500	108100	98.8	96.9
3	-	-	500	DMA	5.9	0.60981	0.0180	2.1	6.89	0.2	6.58	2.432	3.049	0.69	2.20	96	1.21	165100	155600	98.3	95.2
4	-	-	500	NAM	5.9	0.74458	0.0220	2.6	8.42	0.2	6.58	2.970	3.723	1.00	2.70	97	1.32	233600	184600	97.9	93.2
5	-	-	500	DMA	5.9	0.60981	0.0285	3.4	10.90	0.2	6.58	2.428	3.049	1.20	3.50	96	1.38	281200	227300	97.3	90.6

[a] All polymerizations were performed in Water at 70 °C with 120 reaction time per block. The volume ratio of solvent to monomer was maintained at 0.80:0.20. [b] [CTA] refers to the initial equivalents of methyl 2-[methyl(4-pyridinyl)carbamothioylthio]propionate and subsequently the equivalents of macroCTA derived from this CTA. No additional CTA was added during the subsequent block additions. [c] Initiator solution of 100 mg VA-044 in 10 mL H₂O (0.0309 M). [d] Represents the total amount of VA-044 at time t₀ considering the moles of VA-044 added (I_{added}) + the moles of VA-044 remaining (I_{rem}) from the previous block after 2h. I_{rem} = I_{total} - 2fe^{-kd_{th}t} (1-fc/2)^[1]. [e] Conversion was calculated by ¹H NMR. [f] M_n(theory) = ([Monomer]₀/[CTA]₀)^p Mmonomer + M_{CTA}, where [Monomer]₀/[CTA]₀ is the ratio of monomer to CTA at time zero, p is the conversion of polymerization and Mmonomer and M_{CTA} are the molecular weights of the monomer and the CTA.

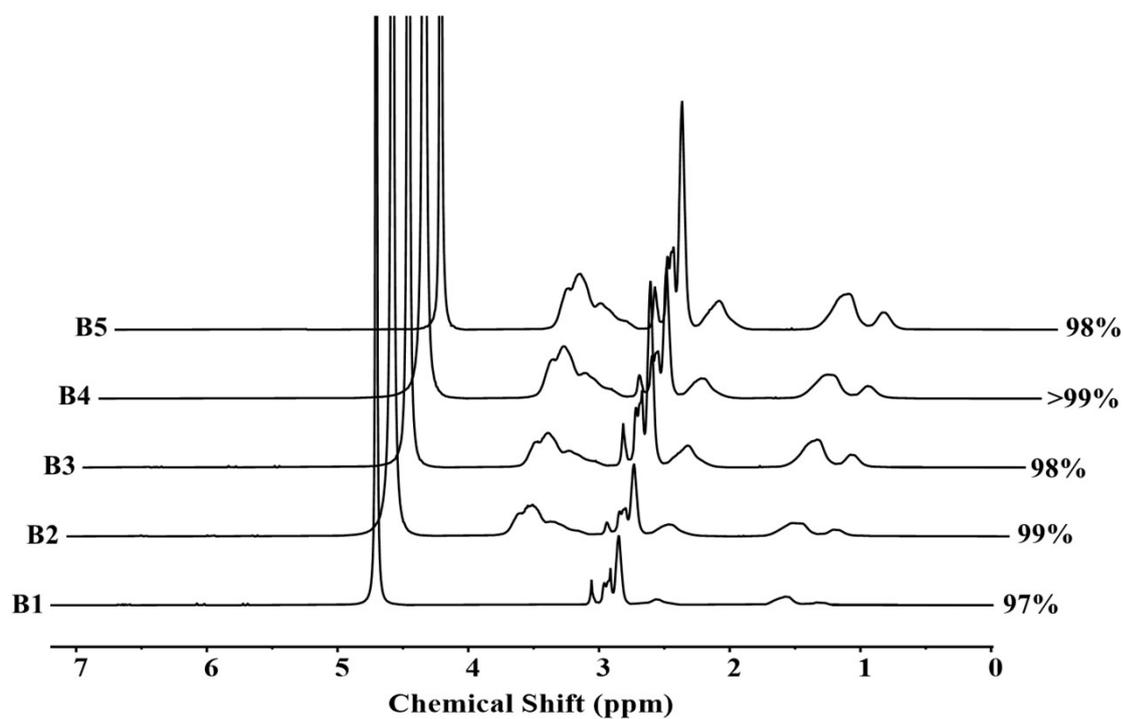


Figure S6. ¹H NMR spectra of P(DMA-b-NAM-b-DMA-b-NAM-b-DMA) pentablock copolymer with DP=200.

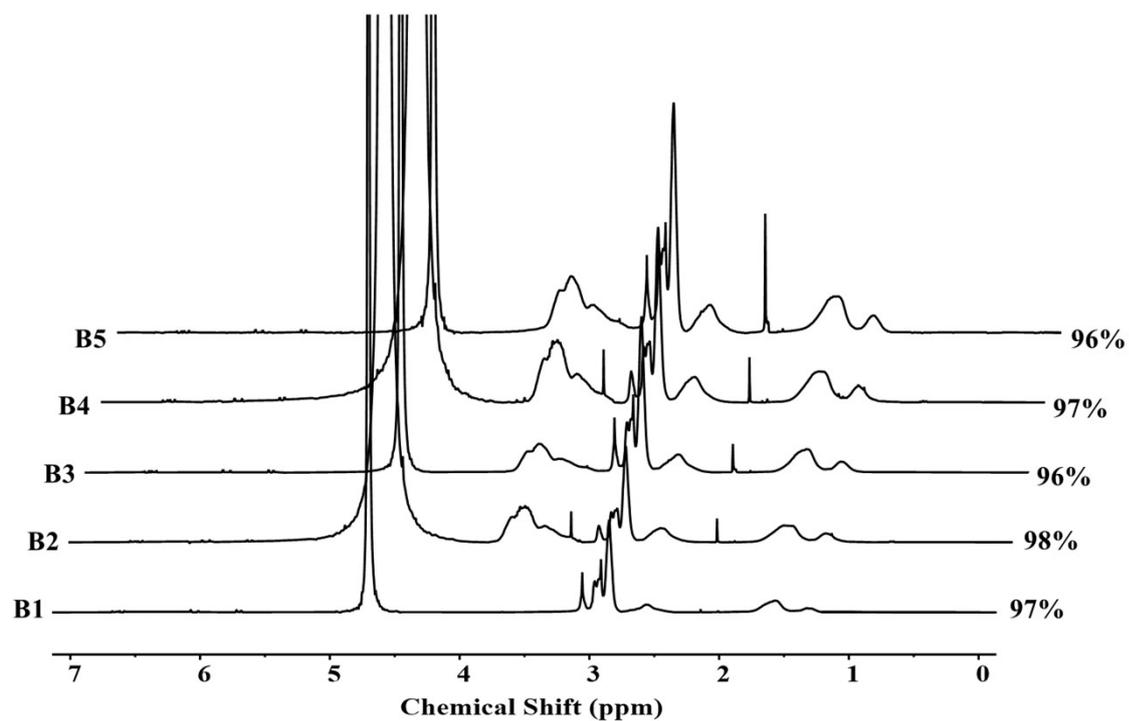


Figure S7. ¹H NMR spectra of P(DMA-b-NAM-b-DMA-b-NAM-b-DMA) pentablock copolymer with DP=500.

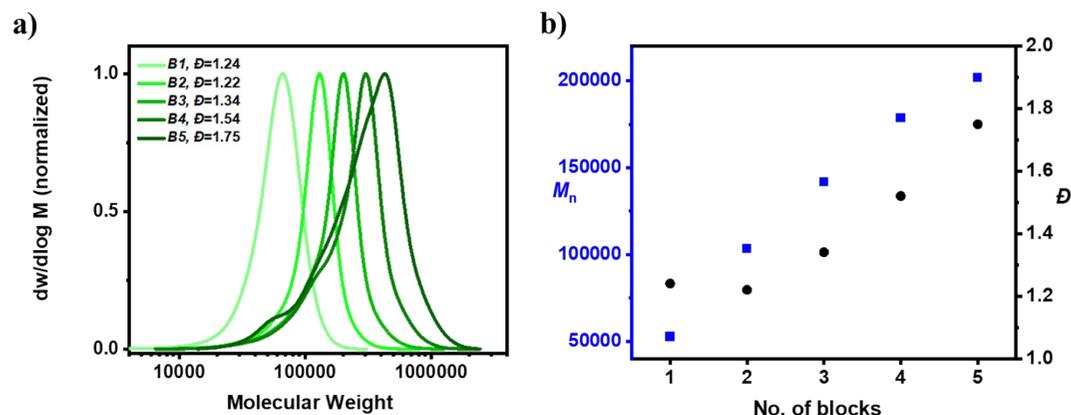


Figure S8. a) SEC traces illustrating the molecular weight distributions for consecutive cycles during the synthesis of a pentablock with DP=500 and CTA 1. b) Evolution of dispersity (black) and the measured molecular weight (blue) during this multiblock synthesis.

Table S7. Experimental conditions and characterization data for the synthesis of P(DMA-b-NAM-b-DMA-b-NAM-b-DMA) pentablock copolymer with DP=500.^[a] Data corresponds to figures X.

No. block	CTA 1 (mg)	CTA (10 ⁻⁵ mol)	DP	M	Monomer (10 ⁻³ mol)	Monomer (mL)	[VA-044]:[CTA] ₀ ^[b]	VA-044 (10 ⁻⁷ mol)	I _{added} (μl) ^[c]	M %	H ₂ SO ₄ (μL)	H ₂ O (mL)	V _{tot} (mL)	I _{rem} (10 ⁻⁸ mol)	I _{tot} (10 ⁻⁷ mol) ^[d]	% Conv. ^[e]	\bar{D}	$M_n^{(Theo)}$ (g mol ⁻¹) ^[f]	$M_n^{(SEC)}$	%L Block	%L Total
1	2.8	1.18	500	DMA	5.9	0.60981	0.0808	9.6	30.9	0.2	-	2.408	3.049		9.60	94	1.24	46900	52700	92.8	92.8
2	-	-	500	NAM	5.9	0.74458	0.0404	4.8	15.5	0.2	-	2.963	3.723	4.33	5.21	96	1.22	114600	103400	96.0	89.1
3	-	-	500	DMA	5.9	0.60981	0.0672	8.0	25.7	0.2	-	2.414	3.049	2.35	8.19	84	1.34	156300	141800	93.8	83.6
4	-	-	500	NAM	5.9	0.74458	0.1212	14.3	46.4	0.2	-	2.932	3.723	3.71	14.71	95	1.54	223300	178600	89.4	74.7
5	-	-	500	DMA	5.9	0.60981	0.1602	19.0	61.3	0.2	-	2.378	3.049	6.66	19.63	93	1.75	269400	202000	86.3	64.5

[a] All polymerizations were performed in Water at 70 °C with 120' reaction time per block. The volume ratio of solvent to monomer was maintained at 0.80:0.20. [b] [CTA] refers to the initial equivalents of 2-(((Butylsulfanyl)carbothiyl)sulfanyl)propanoic acid and subsequently the equivalents of macroCTA derived from this CTA. No additional CTA was added during the subsequent block additions. [c] Initiator solution of 100 mg VA-044 in 10 mL H₂O (0.0309 M). [d] Represents the total amount of VA-044 at time t₀ considering the moles of VA-044 added (I_{added}) + the moles of VA-044 remaining (I_{rem}) from the previous block after 2h. I_{rem} = I_{total} - 2fe^{-k_{dt}} (1-fc/2)^[1]. [e] Conversion was calculated by ¹H NMR. [f] $M_n^{(theory)} = ([Monomer]_0/[CTA]_0)^p \cdot M_{monomer} + M_{CTA}$, where [Monomer]₀/[CTA]₀ is the ratio of monomer to CTA at time zero, p is the conversion of polymerization and M_{monomer} and M_{CTA} are the molecular weights of the monomer and the CTA.

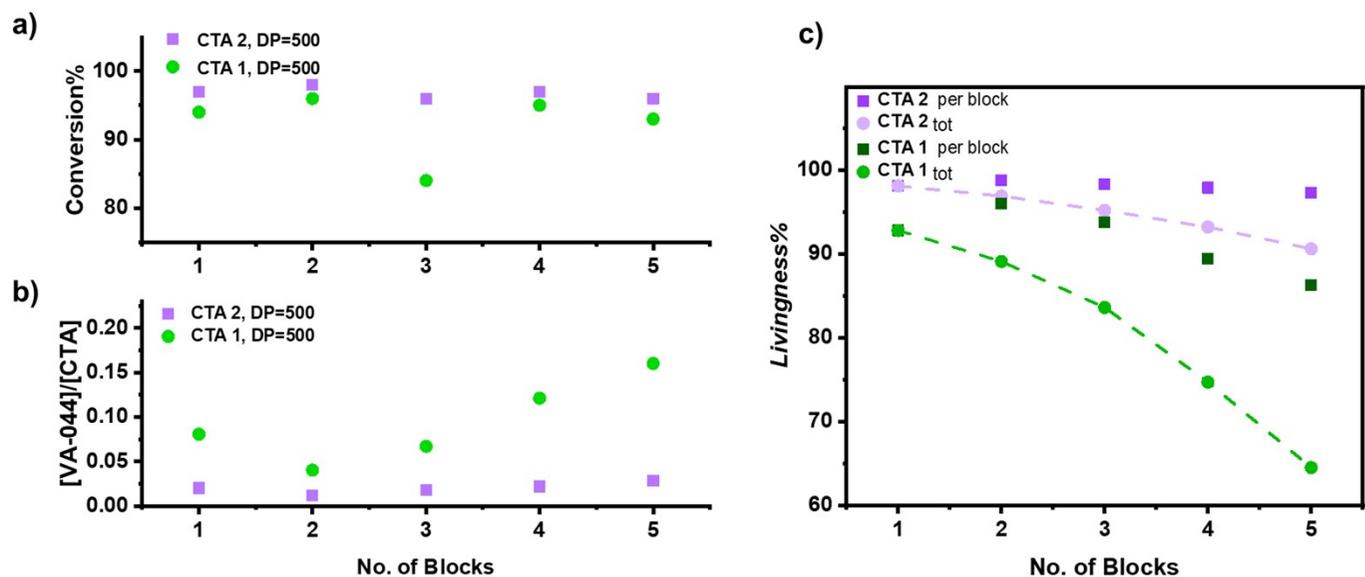


Figure S9. **a)** Conversion per block of pentablock copolymer with DP=500, with switchable CTA 2 (purple) in presence of acid (corresponds to fig.3) and of pentablock copolymer with CTA 1 in absence of acid (green). **b)** Initiator concentration (with respect to the CTA) for each block, that corresponds to the conversion in figure 9a, where purple data points correspond to CTA 2 pentablock copolymer, and green data points correspond to CTA 1 pentablock copolymer. **c)** Livingness per block for CTA 2 pentablock copolymer (dark purple), evolution of total livingness of CTA 2 pentablock copolymer (light purple), livingness per block for CTA 1 pentablock copolymer (dark green) and evolution of total livingness of CTA 1 pentablock copolymer (light green).

Data corresponding to Figure 5

Table S8. Experimental conditions and characterization data for the synthesis of P(NAM-b-DMA-b-NAM-b-DMA-b- NAM-b -DMA-b-NAM-b-DMA-b- NAM-b-DMA-b-NAM-b-DMA-b-NAM-b-DMA-b- NAM-b -DMA-b-NAM-b-DMA-b-NAM-b-DMA) icosablock copolymer with low DP.^[a] Data corresponds to figures X.

No. block	CTA 1 (mg)	CTA (10 ⁻⁵ mol)	DP	M	Monomer (10 ⁻⁴ mol)	Monomer (mL)	[VA-044]:[CTA] ^[b]	VA-044 (10 ⁻⁷ mol)	I _{added} (ul) ^[c]	M%	H ₂ SO ₄ (uL)	H ₂ O (mL)	V _{tot} (mL)	I _{rem} (10 ⁻⁸ mol)	I _{tot} (10 ⁻⁷ mol) ^[d]	% Conv. ^[e]	M _n ^(Theor.) (g mol ⁻¹) ^[f]	M _n ^(SEC)	Đ	%L Block	%L Total
1	31.2	11.54	30	NAM	34.62	0.436	0.0030	3.5	11.19	0.15	6.4	2.457	2.90		3.46	>99.9	4500	3600	1.25	99.8	99.8
2	-	-	6	DMA	6.92	0.0714	0.0017	2.0	6.34	0.2	0.250	0.279	0.36	9.5	2.91	99	5100	4100	1.22	99.9	99.7
3	-	-	6	NAM	6.92	0.0871	0.0011	1.3	4.10	0.2	0.250	0.344	0.44	8.0	2.08	>99.9	5900	4700	1.19	99.9	99.5
4	-	-	6	DMA	6.92	0.0714	0.0021	2.4	7.83	0.2	0.250	0.278	0.36	5.7	2.99	97	6500	5200	1.18	99.8	99.3
5	-	-	6	NAM	6.92	0.0871	0.0012	1.4	4.48	0.2	0.250	0.344	0.44	8.2	2.21	98	7300	5700	1.17	99.9	99.2
6	-	-	6	DMA	6.92	0.0714	0.0021	2.4	7.83	0.2	0.250	0.278	0.36	6.1	3.01	98	7900	6100	1.16	99.9	99.1
7	-	-	6	NAM	6.92	0.0871	0.0015	1.7	5.60	0.2	0.250	0.343	0.44	8.3	2.57	99	8800	6600	1.16	99.8	98.9
8 ^[g]	-	-	6	DMA	3.46	0.0357	0.0024	1.7	4.48	0.2	0.125	0.138	0.18	3.6	1.74	97	9300	7200	1.14	99.8	98.7
9	-	-	6	NAM	3.46	0.0436	0.0015	1.7	2.80	0.2	0.125	0.171	0.22	4.8	1.35	99	10200	7800	1.13	99.8	98.4
10	-	-	6	DMA	3.46	0.0357	0.0023	2.7	4.29	0.2	0.125	0.139	0.18	3.7	1.70	98	10800	8800	1.13	99.8	98.3
11	-	-	6	NAM	3.46	0.0436	0.0016	1.8	2.99	0.2	0.125	0.171	0.22	4.7	1.39	99	11600	9500	1.13	99.9	98.1
12	-	-	6	DMA	3.46	0.0357	0.0022	2.8	4.11	0.2	0.125	0.139	0.18	3.9	1.65	99	12200	10400	1.13	99.8	97.9
13	-	-	6	NAM	3.46	0.0436	0.0033	3.8	6.16	0.2	0.125	0.168	0.22	4.6	2.36	98	13000	11400	1.13	99.7	97.6
14	-	-	6	DMA	3.46	0.0357	0.0042	4.8	7.84	0.2	0.125	0.135	0.18	6.5	3.08	>99.9	13600	12300	1.14	99.7	97.2
15	-	-	6	NAM	3.46	0.0436	0.0031	3.6	5.78	0.2	0.125	0.169	0.22	8.5	2.64	99	14500	13500	1.13	99.7	96.9
16	-	-	6	DMA	3.46	0.0357	0.0043	5.0	8.02	0.2	0.125	0.135	0.18	7.5	3.21	98	15000	14300	1.15	99.6	96.6
17	-	-	6	NAM	3.46	0.0436	0.003	3.5	5.60	0.2	0.125	0.169	0.22	9.0	2.62	99	15900	15500	1.14	99.7	96.2
18	-	-	6	DMA	3.46	0.0357	0.0043	5.0	8.02	0.2	0.125	0.135	0.18	7.1	3.20	>99.9	16500	16700	1.15	99.6	95.8
19	-	-	6	NAM	3.46	0.0436	0.0033	3.8	6.16	0.2	0.125	0.168	0.22	9.1	2.79	99	17300	17000	1.15	99.7	95.5
20	-	-	6	DMA	3.46	0.0357	0.003	3.5	5.60	0.2	0.125	0.137	0.18	7.4	2.50	99	17900	17600	1.17	99.7	95.2

[a] All polymerizations were performed in Water at 70 °C with 120' reaction time per block. The volume ratio of solvent to monomer was maintained at 0.80:0.20. [b] [CTA] refers to the initial equivalents of methyl 2-[methyl(4-pyridinyl)carbamothioylthio]propionate and subsequently the equivalents of macroCTA derived from this CTA. No additional CTA was added during the subsequent block additions. [c] Initiator solution of 100 mg VA-044 in 10 mL H₂O (0.0309 M). [d] Represents the total amount of VA-044 at time t₀ considering the moles of VA-044 added (I_{added}) + the moles of VA-044 remaining (I_{rem}) from the previous block after 2h. I_{rem} =

$I_{\text{total}} \propto 2fe^{-kd_{\text{tr}}} (1-fc/2)^{[1]}$. [e] Conversion was calculated by $^1\text{H NMR}$. [f] $M_{n(\text{theory})} = ([\text{Monomer}]_0/[\text{CTA}]_0) p \propto M_{\text{monomer}} + M_{\text{CTA}}$, where $[\text{Monomer}]_0/[\text{CTA}]_0$ is the ratio of monomer to CTA at time zero, p is the conversion of polymerization and M_{monomer} and M_{CTA} are the molecular weights of the monomer and the CTA. [g] Half of the quantity was removed from the vial.

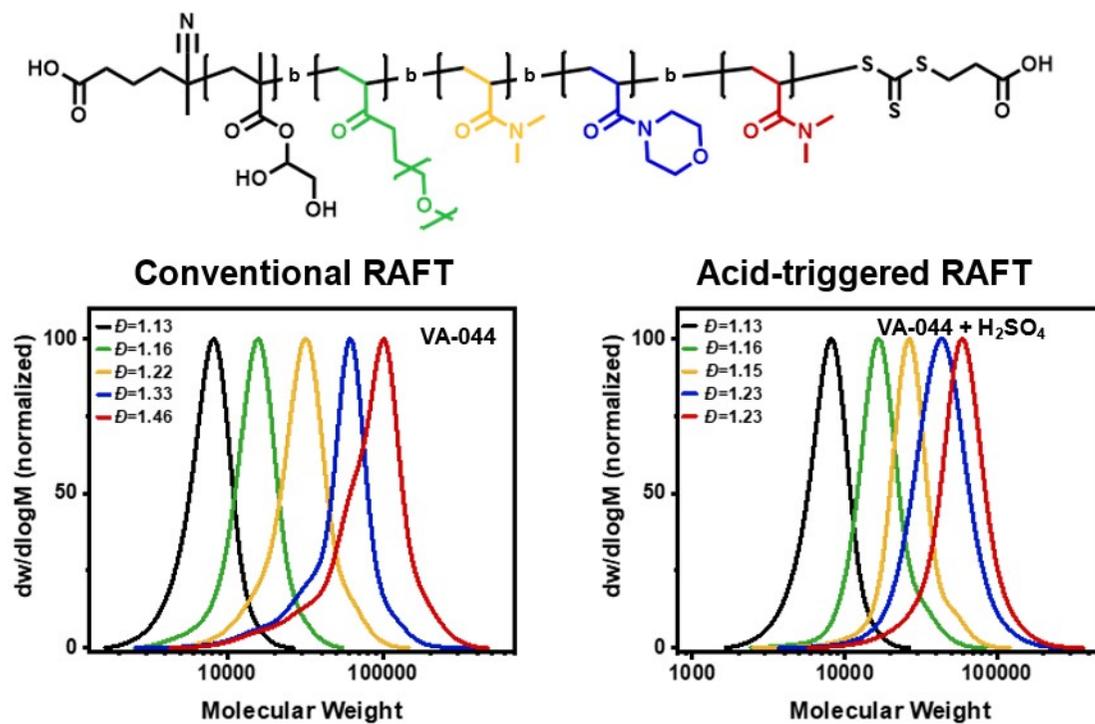


Figure S10. Pentablock copolymers synthesized with conventional RAFT versus acid-triggered RAFT.

Table S9. Experimental conditions and characterization data for the synthesis of P(GDMA-b-PPEGA₄₈₀-b-DMA-b- NAM-b -DMA) pentablock copolymer .^[a] Data corresponds to Figure S10.

No. block	CTA 3 ^[b] (mg)	CTA (10 ⁻⁵ mol)	DP	M	Monomer (10 ⁻³ mol)	Monomer (mL)	[VA-044]:[CTA] ^[c]	VA-044 (10 ⁻⁷ mol)	I _{added} (ul) ^[d]	M%	H ₂ SO ₄ (uL)	H ₂ O (mL)	% Conv. ^[f]	Đ	M _n ^(Theo.) (g mol ⁻¹) ^[g]	M _n ^(SEC)
1	7.5	2.44	15	GMA	0.37	0.52	0.015	3.7	11.8	20	0.7	-	>99	1.13	2700	8100
2	-	-	15	PGEA ₄₈₀	0.37	0.16	0.018	4.4	14.2	20	1.5	0.62	97	1.16	9700	15700
3	-	-	75	DMA	1.83	0.19	0.011	2.7	8.7	20	1.0	0.73	95	1.15	16700	24700
4	-	-	75	NAM	1.83	0.23	0.01	2.4	7.9	20	1.5	0.91	>99	1.23	27300	37800
5	-	-	75	DMA	1.83	0.19	0.013	3.2	10.3	20	1.0	0.73	98	1.23	34600	51300

[a] All polymerizations were performed in Water at 70 °C with 120 reaction time per block. The volume ratio of solvent to monomer was maintained at 0.80:0.20.[b] CTA 3 refers to 4-(((2-Carboxyethyl)thio)carbonothioyl)thio)-4-cyanopentanoic acid [c] [CTA] refers to the initial equivalents of methyl 2-[methyl(4-pyridinyl)carbamothioylthio]propionate and subsequently the equivalents of macroCTA derived from this CTA. No additional CTA was added during the subsequent block additions. [d] Initiator solution of 100 mg VA-044 in 10 mL H₂O (0.0309 M). [e] Represents the total amount of VA-044 at time t₀ considering the moles of VA-044 added (I_{added}) + the moles of VA-044 remaining (I_{rem}) from the previous block after 2h. I_{rem} = I_{total} - 2fe^{-k_{dt}t} (1-fc/2)^[1]. [f] Conversion was calculated by ¹H NMR. [g] M_n(theory) = ([Monomer]₀/[CTA]₀) p / Mmonomer + M_{CTA}, where [Monomer]₀/[CTA]₀ is the ratio of monomer to CTA at time zero, p is the conversion of polymerization and Mmonomer and M_{CTA} are the molecular weights of the monomer and the CTA.

Table S10. Experimental conditions and characterization data for the synthesis of P(GDMA-b-PPEGA₄₈₀-b-DMA-b- NAM-b -DMA) pentablock copolymer .^[a] Data corresponds to Figure S10.

No. block	CTA 3 ^[b] (mg)	CTA (10 ⁻⁵ mol)	DP	M	Monomer (10 ⁻³ mol)	Monomer (mL)	[VA-044]:[CTA] ^[c]	VA-044 (10 ⁻⁷ mol)	I _{added} (ul) ^[d]	M%	H ₂ SO ₄ (uL)	H ₂ O (mL)	% Conv. ^[f]	Đ	M _n ^(Theo.) (g mol ⁻¹) ^[g]	M _n ^(SEC)
1	7.5	2.44	15	GMA	0.37	0.52	0.022	5.37	17.4	20	-	-	98	1.13	2700	7000
2	-	-	15	PGEA ₄₈₀	0.37	0.16	0.030	7.32	23.7	20	-	0.62	98	1.16	9700	13600
3	-	-	75	DMA	1.83	0.19	0.022	5.37	17.4	20	-	0.73	99	1.22	17100	26500
4	-	-	75	NAM	1.83	0.23	0.018	4.39	14.2	20	-	0.91	99	1.33	27600	43800
5	-	-	75	DMA	1.83	0.19	0.029	7.08	22.9	20	-	0.73	97	1.46	34700	62100

[a] All polymerizations were performed in Water at 70 °C with 120 reaction time per block. The volume ratio of solvent to monomer was maintained at 0.80:0.20.[b] CTA 3 refers to 4-(((2-Carboxyethyl)thio)carbonothioyl)thio)-4-cyanopentanoic acid [c] [CTA] refers to the initial equivalents of methyl 2-[methyl(4-pyridinyl)carbamothioylthio]propionate and subsequently the equivalents of macroCTA derived from this CTA. No additional CTA was added during the subsequent block additions. [d] Initiator solution of 100 mg VA-044 in 10 mL H₂O (0.0309 M). [e] Represents the total amount of VA-044 at time t₀ considering the moles of VA-044 added (I_{added}) + the moles of VA-044 remaining (I_{rem}) from the previous block after 2h. I_{rem} = I_{total} - 2fe^{-k_{dt}t} (1-fc/2)^[1]. [f] Conversion was calculated by ¹H NMR. [g] M_n(theory) = ([Monomer]₀/[CTA]₀) p / Mmonomer + M_{CTA}, where [Monomer]₀/[CTA]₀ is the ratio of monomer to CTA at time zero, p is the conversion of polymerization and Mmonomer and M_{CTA} are the molecular weights of the monomer and the CTA.

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- [1] Gody, G., Maschmeyer, T., Zetterlund, P. B. & Perrier, S. Rapid and quantitative one-pot synthesis of sequence-controlled polymers by radical polymerization. *Nature communications* **4**, 2505 (2013).