Supplementary Information for

Putting the RAFT in GRAFT: Intermolecular Graft Exchange Between Bottlebrush Polymers Using Reversible Addition-Fragmentation Chain Transfer

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1 Instrumental methods

1.1 Atomic Force Microscopy

Samples were prepared by drop-casting a 0.005 mg/ml polymer solution in chloroform onto freshly cleaved mica and drying under a gentle N_2 flow for 10 s. Images were collected directly after sample preparation using a Bruker Dimension Icon instrument with ScanAsyst in Air, PeakForce tapping and ScanAsyst-Air probes. Images were processed with Gwyddion software.

1.2 Nuclear Magnetic Resonance Spectroscopy

^{1}H Nuclear Magnetic Resonance (NMR) spectra and ^{1}H-^{13}C Heteronuclear Single Quantum Coherence (HSQC) spectra were recorded in chloroform-d ($CDCl_3$) or methanol-d_4 (CD_3OD) on Bruker Avance III HD (300 MHz or 400 MHz) spectrometer at 300 K. Chemical shift values (δ) are reported in ppm. Solvent residual signals were used for calibration.

1.3 Size Exclusion Chromatography

SEC was carried out using the instrument setups and solvent conditions listed in Table S1. All analyte samples were filtered through a syringe filter prior to injection. Experimental molar mass ($M_{n,SEC}$) and dispersity ($Đ$) values were determined by employing conventional calibration with poly(methyl methacrylate) (PMMA) standards (Agilent EasyVials) using Agilent GPC/SEC software.

Table S1 SEC instrument conditions.

	DMF	**$CHCl_3$**
Instrument	Agilent Infinity II MDS	Agilent Infinity II MDS
Detectors [A]	DRI, VS, DALS, single-wavelength UV	DRI, VS, DALS, multi-wavelength UV
Guard column	PLgel 5 µm	PLgel 5 µm
Analytical columns	2 x PLgel Mixed D 300 x 7.5 mm, 200-400,000 g/mol linear operating range [B]	2 x PLgel Mixed C 300 x 7.5 mm, 200-2,000,000 g/mol linear operating range [B]
Calibration [C]	PMMA 500-900,000 g/mol	PMMA 600-2,200,000
Eluent	DMF + 5 mmol NH_4BF_4	$CHCl_3$ (no additives)
Sample filter	Nylon membrane, 0.22 µm pore size	PTFE membrane, 0.22 µm pore size
Flow rate	1 ml/min	1 ml/min
Temperature	50 °C	30 °C

[A] DRI, VS and DALS stand for differential refractive index, viscometry and dual-angle light scattering (15° and 90°) detectors, respectively.
[B] Polystyrene equivalent.
[C] Calibration range is given as a representative example on a given month.

2 Materials

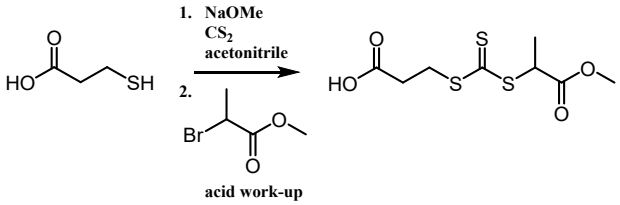
Acetonitrile (Sigma), 4,4'-azobis(4-cyanovaleric acid) (ACVA, 98%, Alfa Aesar), carbon disulfide (CS_2, ≥99.9%), 1,4-dioxane (≥99%, Sigma-Aldrich), dichloromethane anhydrous (DCM, 99.8%, Sigma-Aldrich), *N,N*-Dicyclohexylcarbodiimide (DCC, 99%, Acros Organics), 4-(dimethylamino)pyridine (DMAP, ≥99.0%, Alfa Aesar), diethyl ether (≥99.8%, Sigma-Aldrich), *N,N*-dimethylformamide (DMF, HPLC-grade, Merck), magnesium sulfate (drying agent, anhydrous, Sigma-Aldrich), methanol (≥99.9%, HPLC grade, Sigma-Aldrich), methyl 2-bromopropionate (99%, Acros Organics), 3-mercaptopropionic acid (99+%, Acros Organics), methanol-d_4 (CD_3OD, 99.8 atom% D, Sigma-Aldrich), chloroform-d ($CDCl_3$, 99.8 atom% D, Sigma-Aldrich), oxalyl chloride solution (2.0 M in methylene chloride, Sigma-Aldrich), 1-pyrenebutanol (99%, Sigma-Aldrich), sodium methoxide solution (25 wt% in methanol, Sigma Aldrich), were used as received from the supplier. 2-Hydroxyethyl acrylate (HEA, ≥96%, Sigma-Aldrich) and 4-acryloylmorpholine (NAM, 97%, Sigma-Aldrich) were passed through aluminium oxide (activated, basic, Brockman I standard grade) to remove the inhibitor. 2-(((Butylthio)carbonothioyl)thio)propanoic acid (PABTC) was synthesised according to literature[1] and recrystallised twice from hexane before use.

Blue LED lights (exact wavelength not known) were purchased from Amazon.com and attached around the inner surface of a metal mesh cylinder (Ø=8 cm) (Figure S1). Vials containing the reaction mixtures were placed at the bottom of the holder at roughly 4 cm distance from the light source. The reactor was placed inside a fume hood under 0.5 m/s air flow. The temperature was controlled using a cardboard housing and measure[illegible]h the bottom of the reactor.

Figure S1. LED reactor used for photoiniferter reactions.

3 Synthesis and characterisation of materials

3.1 Synthesis of 3-((((1-methoxy-1-oxopropan-2-yl)thio)carbonothioyl)thio)propanoic acid (MPPATC)



Scheme S1 Reaction scheme for the preparation of the Z group functional RAFT agent used in the functionalisation of pHEA.

In a 500 ml round-bottom flask immersed in an ice bath, mercaptopropionic acid (12.3 ml, 0.14 mol, 1.0 equiv.) was dissolved in acetonitrile (250 ml) and sodium methoxide solution (25 wt% sol. in methanol) (66 ml, 0.29 mol, 2.1 equiv.) was added dropwise. After 5 min, carbon disulfide (9.3 ml, 0.16 mol, 1.1 equiv.) was added dropwise to the reaction mixture, the flask was removed from the ice bath and stirring was continued at room temperature for 1 h. Methyl 2-bromopropionate (17.4 ml, 0.16 mol, 1.1 equiv.) was added over cooling and stirring was continued at room temperature overnight.

The product was isolated by adding concentrated HCl (1.5 equiv.) to the stirred reaction mixture, followed by the addition of deionized water until an oil separated. The oil was dried over magnesium sulfate in DCM and volatiles were removed with rotary evaporation (30 °C) to give the product as an orange oil. The structure was confirmed by ^{1}H NMR spectroscopy in $CDCl_3$ (Figure S1). The product was used for functionalisation without further purification.

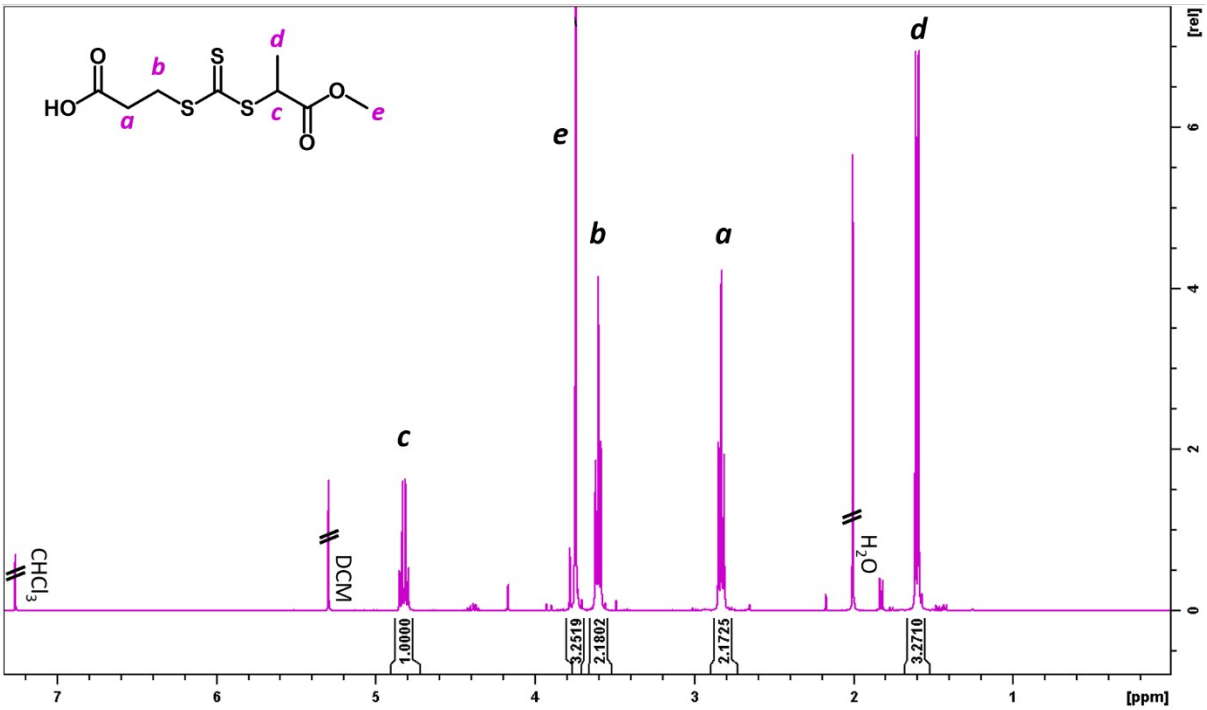
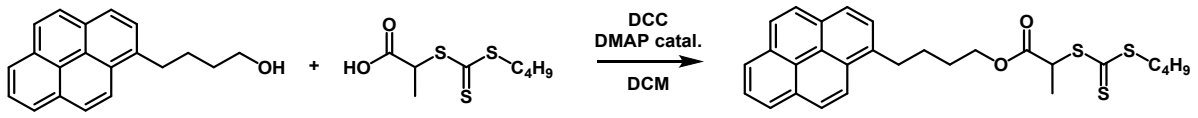


Figure S2. ^{1}H NMR spectrum of the synthesised RAFT agent, MPPATC ($CDCl_3$).

3.2 Synthesis of 4-(pyren-1-yl)butyl 2-(((butylthio)carbonothioyl)thio)propanoate (pyr-PBTC)



Scheme S2 Reaction scheme for the synthesis of pyrene-functional RAFT agent, pyr-PBTC.

1-Pyrenebutanol (250 mg, 0.911 mmol) and PABTC (239 mg, 1.00 mmol) were dissolved in anhydrous DCM (5 ml) under nitrogen and cooled with an ice bath. DMAP (1.11 mg, 0.091 mmol) and then DCC (216 mg, 1.05 mmol) were added to the reaction mixture and the mixture was stirred overnight at room temperature. Solids were filtered off, the solution was passed through a silica plug using a hexane/ethyl acetate (2:1) eluent and volatiles were removed with a rotary evaporator to give a yellow oil (440 mg, 97%).

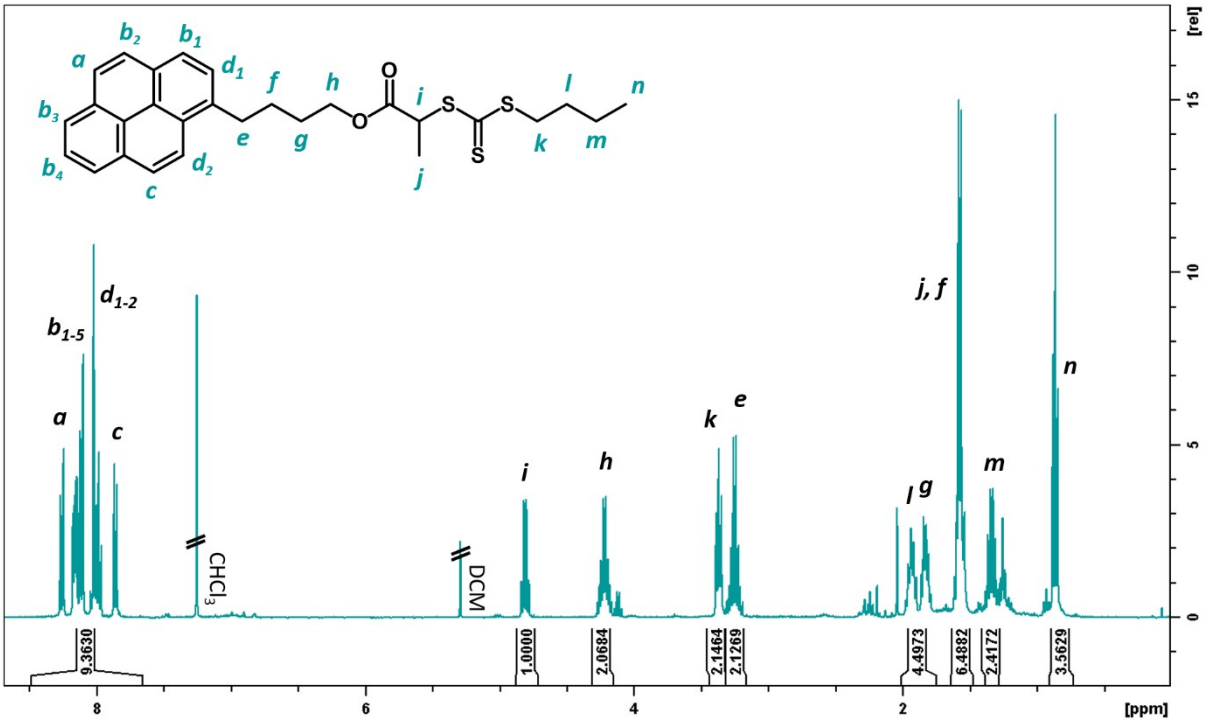
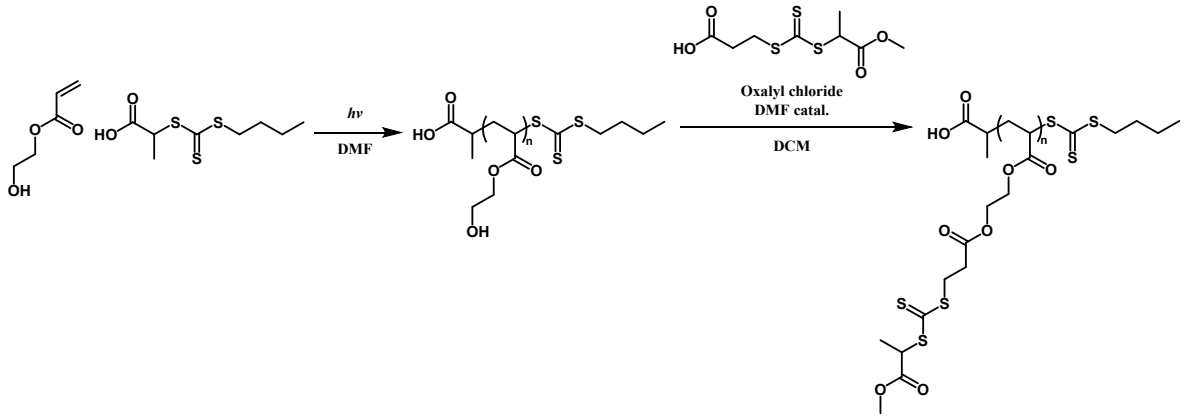


Figure S3. ^{1}H NMR spectrum of the pyrene-functionalised RAFT agent, pyr-PBTC ($CDCl_3$).

3.3 Synthesis of MPPATC-functionalised poly(2-hydroxyethyl acrylates) (pCTAs)



Scheme S3. Synthesis of MPPATC-functionalised poly(2-hydroxyethyl acrylate) backbones.

To prepare functionalised $pHEA_{133}$, PABTC (39.9 mg, 0.167 mmol) and HEA (3.22 g, 27.7 mmol) were weighed into a 25 ml vial and dissolved in DMF (13.1 g, $[M]_0$=2 M). A sample was taken for ^{1}H NMR analysis. The vial was sealed with a rubber septum and the solution was deoxygenated by bubbling nitrogen gas into the solution for 15 min. Polymerisation was carried out over 15 h by subjecting the vial to blue LED irradiation (20-30 °C). Samples were taken after the reaction for SEC analysis in DMF and ^{1}H NMR analysis in CD_3OD.

A fraction of the reaction mixture (7.4 mmol -OH, 1 equiv.) was transferred into a dry round-bottom flask and anhydrous DMF was added. In a separate dry round-bottom flask, MPPATC (3.00 g, 11.2 mmol, 1.5 equiv.) was dissolved in anhydrous DCM and oxalyl chloride (1.1 ml, 13 mmol, 1.8 equiv.) and anhydrous DMF (2 drops) were added. Solution was stirred for 1 h and volatiles were removed under vacuum. The residue was redissolved in anhydrous DMF and added dropwise to the polymer solution. Stirring was continued overnight.

The reaction mixture was concentrated, and the polymer was collected through precipitation into methanol followed by centrifugation. The polymer was further redissolved in DCM, reprecipitated twice and dried under vacuum to yield a yellow tacky product.

Conversion of HEA was determined by ^{1}H NMR spectroscopy in CD_3OD using monomer -C**H$_2$**OH signal (δ=3.76) as a reference and by monitoring the disappearance of vinyl protons (δ=5.90 ppm). The mean degree of polymerisation was calculated as

$$DP_p = \frac{[HEA]_0}{[PABTC]_0} p_{HEA} \qquad (S1)$$

and the theoretical number-average molar masses ($M_{n,th}$) as

$$M_{n,th} = M_{PABTC} + DP_p M_{HEA} + DP_p M_{MPPATC} \qquad (S2)$$

where $[HEA]_0$ and $[CTA]_0$ are the initial HEA and CTA concentrations, respectively, p is the monomer conversion as determined by ^{1}H NMR spectroscopy and M_{HEA}, M_{PABTC} and M_{MPPATC} are the molar masses of HEA, PABTC and MPPATC, respectively.

Table S2 Structural information and characterisation details of pHEA backbones before and after functionalisation.

	Structure [A]	Conversion [B] %	DP_p [C]	$M_{n,th}$ [D] (g/mol)	$M_{n,SEC}$ [E] (g/mol)	$Đ$ [E]
.1	$pHEA_{23}$	60	23	2,900	11,800	1.07
.2	$pHEA_{133}$	85	133	48,800	23,300	1.23
.3	$pHEA_{300}$	91	300	35,100	56,400	1.08
1	$pCTA_{23}$	-	23	8,700	12,800	1.14
2	$pCTA_{133}$	-	133	48,800	29,500	1.14
3	$pCTA_{300}$	-	300	110,000	75,600	1.11

[A] Degree of polymerisation was calculated from conversion (Eq. S1) as given by ^{1}H NMR in CD_3OD.
[B] Determined by ^{1}H NMR in CD_3OD.
[C] Theoretical number-average molar mass calculated from conversion (Eq. S2).
[D] Experimental number-average molar mass and dispersity as given by DMF SEC with DRI detection and PMMA calibration.

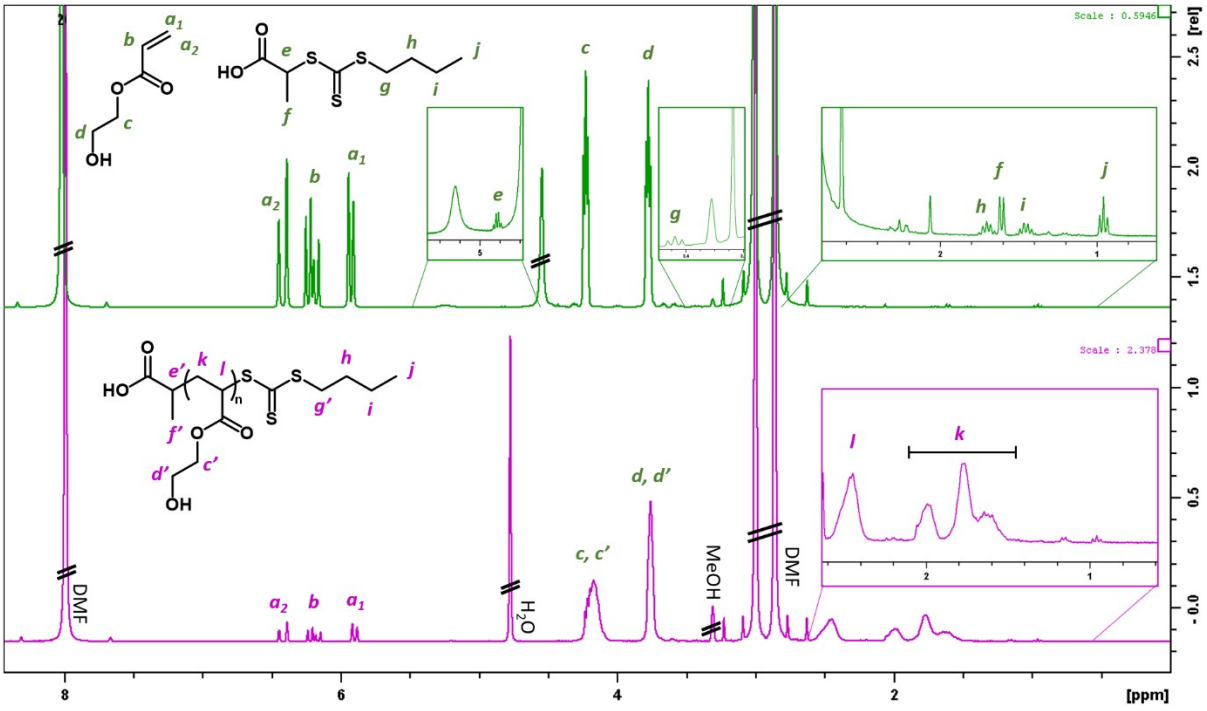


Figure S4. ^{1}H NMR analysis of the RAFT polymerisation of 2-hydroxyethyl acrylate at t = 0 (top) and after the reaction (bottom). Spectra were acquired CD_3OD.

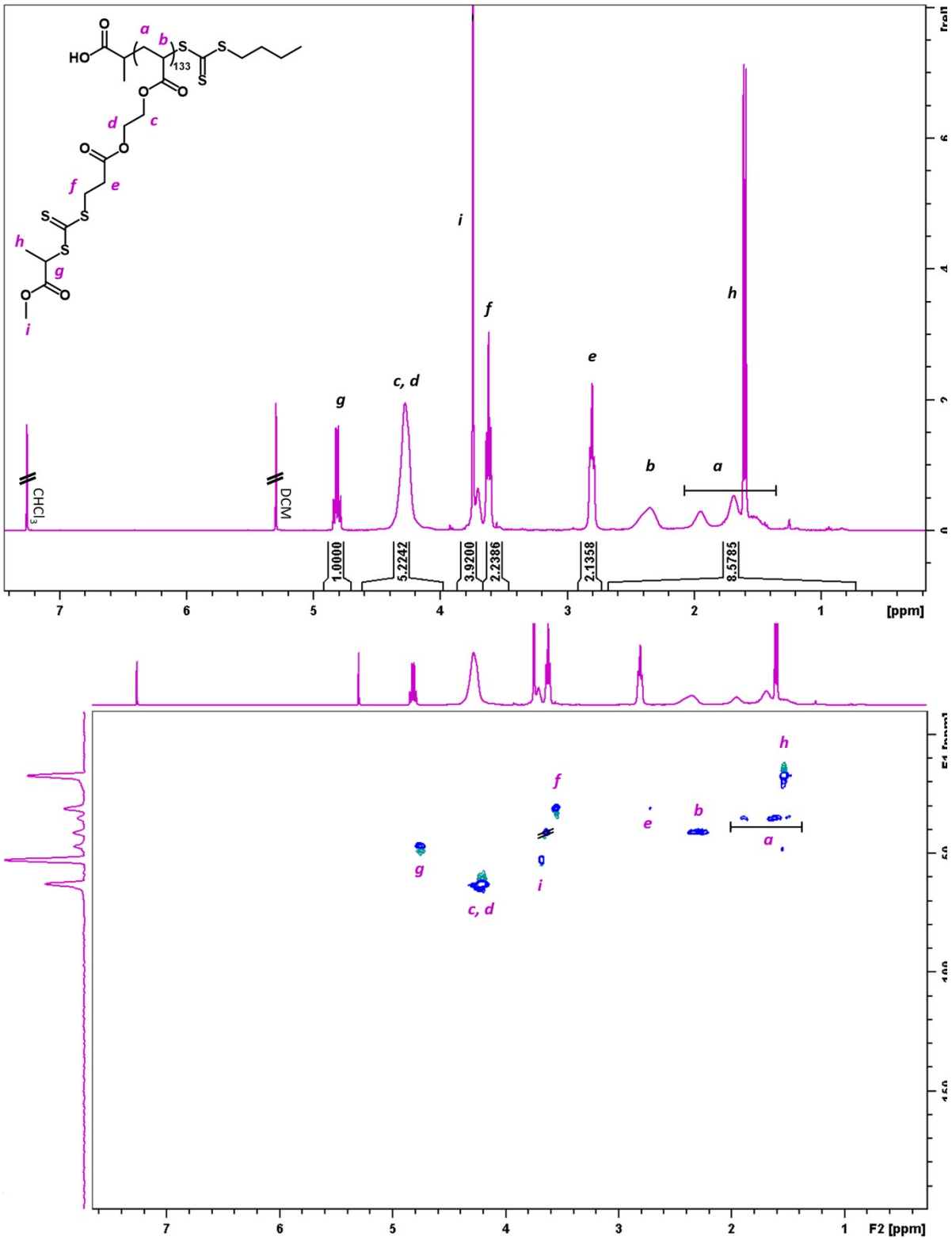


Figure S5. ^{1}H NMR (top) and ^{1}H-^{13}C HSQC (bottom) spectra of MPPATC-functionalised $pHEA_{133}$ in $CDCl_3$.

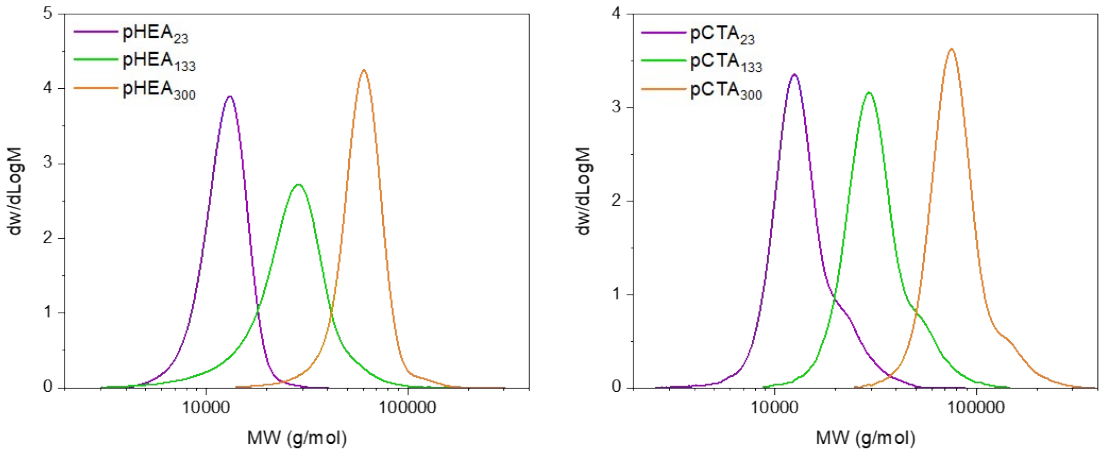
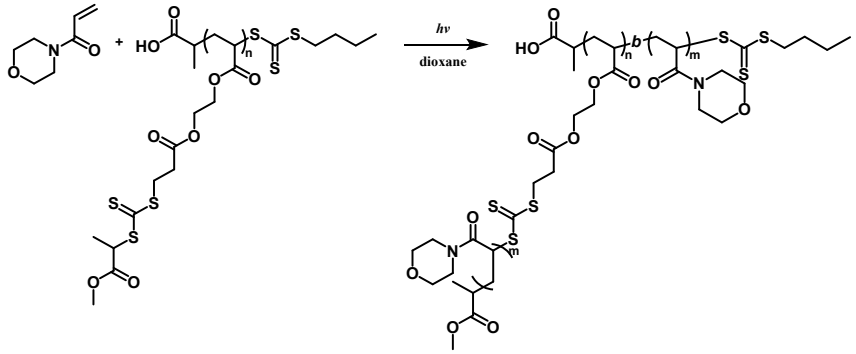


Figure S6. SEC profiles of pHEA backbones before (left) and after functionalisation with MPPATC (right). Analysis was carried out in DMF with DRI detection and PMMA calibration. MW profiles of pCTAs show a high-MW shoulder, likely due to a side reaction of HEA repeat units with oxalyl chloride to form the oxalic acid ester.[2]

3.4 Photoiniferter RAFT polymerisation of graft copolymers



Scheme S4. Photoiniferter RAFT polymerisation of 4-acryloylmorpholine using the Z group approach with functionalised poly(2-hydroxyethyl acrylate) backbones.

The following general procedure was used for polymerising graft copolymer side chains. For preparing $pHEA_{133}$-*graft*-$pNAM_8$ (**2a**), functionalised $pHEA_{133}$ (**2**) (49.76 mg, 0.136 mmol) and NAM (240.34 mg, 1.70 mmol) were weighed in a 2 ml vial. Dioxane (1.55 ml, $[M]_0$ = 1 M) and DMF (30 µl) were added, and sealed vial was left on a stirring plate to solubilise reactants. A sample as taken for ^{1}H NMR analysis and the vial was sealed again with a septum cap and purged with nitrogen for 10 min. Polymerisation was carried out by placing the vial under blue LED light for 3 h. Samples were taken after reaction for SEC analysis in DMF and ^{1}H NMR analysis in $CDCl_3$.

The polymer was precipitated in diethyl ether, collected by centrifugation, redissolved in DCM and reprecipitated twice to remove residual monomer. The product was dried in a vacuum oven (38 °C, 30 min) to give a pale yellow powder.

To remove the linear by-product (terminated grafts), 120 mg of polymer was dissolved in DCM (10 mg/ml) in a 15 ml centrifuge tube. While agitating on a vortex mixer, diethyl ether was added dropwise until polymer separated from the solution. After centrifugation the supernatant was discarded, and the pellet was redissolved in DCM to repeat the procedure. The glassy polymer was redissolved in DCM, precipitated into diethyl ether and vacuum dried (38 °C, 30 min) to give a pale yellow powder (90 mg, 75%).

Conversion of NAM was determined by ^{1}H NMR spectroscopy in $CDCl_3$ using DMF as an internal standard (δ=2.81-2.97 ppm) and by monitoring the disappearance of vinyl protons (δ=5.68 ppm). The mean DP of grafts was calculated as

$$DP_p = \frac{[NAM]_0}{[MPPATC]_0} p_{NAM} \qquad (S3)$$

and theoretical number-average molar masses ($M_{n,th}$) as

$$M_{n,th} = M_{pCTA} + DP_{polyCTA} DP_p M_{NAM} \qquad (S4)$$

where $[NAM]_0$ and $[TTC]_0$ are the initial NAM and side chain MPPATC concentrations, respectively, p is the monomer conversion as determined by ^{1}H NMR spectroscopy and M_{pCTA} and M_{NAM} are the molar masses of the polyCTA and NAM, respectively.

Table S3 Graft copolymers employed in this work.

	Structure	Conversion [A] %	DP_p [B]	m_T [C] (%)	n_{rel} [D] $\cdot 10^3$	$M_{n,th}$ [E] (g/mol)	$M_{n,SEC}$ [F] (g/mol)	$Đ$ [F]
1a	$pHEA_{23}$-*graft*-$pNAM_{10}$	98	10	8	8	41,100	28,000	1.14
1b	$pHEA_{23}$-*graft*-$pNAM_{87}$	85	87	30	4	285,000	178,000	1.56
2a	$pHEA_{133}$-*graft*-$pNAM_{8}$	64	8	≤ 2	≤ 3	189,000	56,700	1.32
2b	$pHEA_{133}$-*graft*-$pNAM_{29}$	82	29	4	1	562,000	157,000	1.34
3a	$pHEA_{300}$-*graft*-$pNAM_{50}$	80	50	20	4	2,230,000	548,000	1.43
3b	$pHEA_{300}$-*graft*-$pNAM_{35}$	85	35	9	3	1,590,000	368,000	1.51

[A] Determined by ^{1}H NMR in $CDCl_3$.

[B] Mean DP of the grafts was calculated from conversion (Eq. S3).

[C] Mass percent of terminated grafts in the crude product as given by RI vs RT data.

[D] Relative number of terminated chains determined from RI vs RT plots as $n_{rel} = (A_T/A_{tot})/DP$

[E] Theoretical number-average molar mass calculated from conversion (Eq. S4).

[F] Experimental number-average molar mass and dispersity as given by SEC analysis in DMF with DRI detection and PMMA calibration.

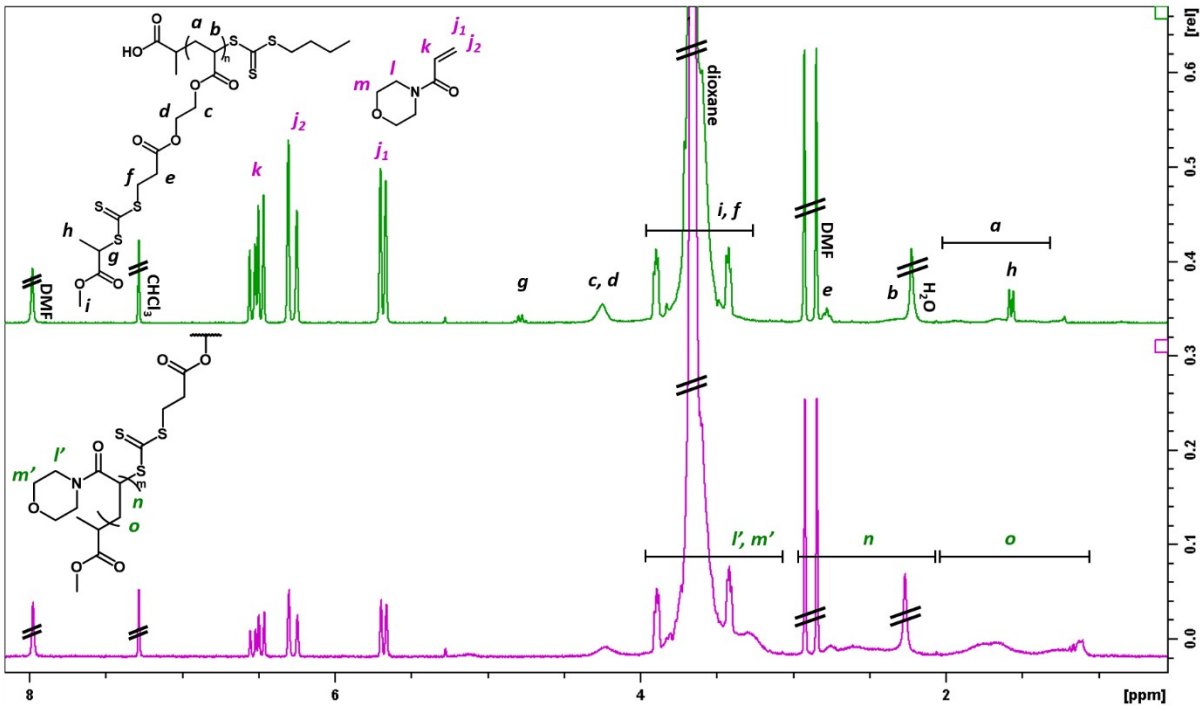


Figure S7. Representative ^{1}H NMR spectra ($CDCl_3$) for the polymerisation of 4-acryloylmorpholine side chains.

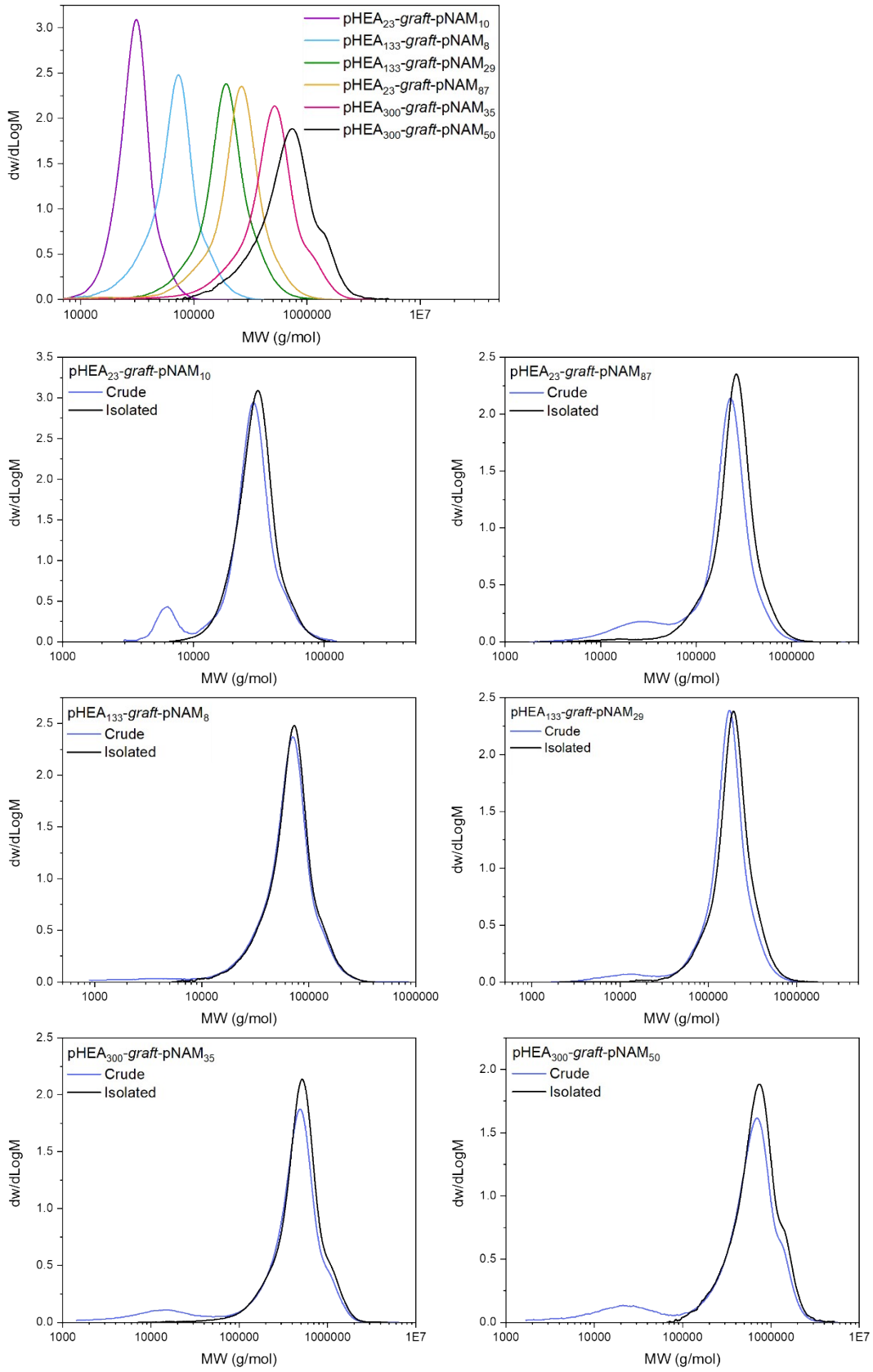
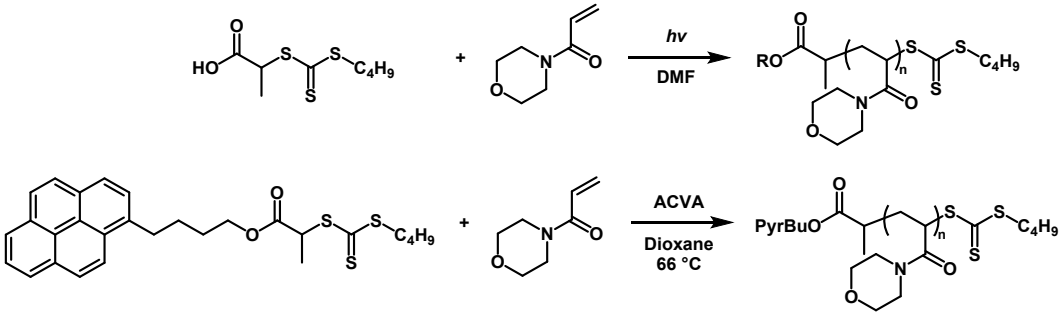


Figure S8. Size exclusion chromatograms of bottlebrush polymers before and after removing terminated side chains. Analysis was carried out in DMF with DRI detection and PMMA calibration.

3.5 Synthesis of linear poly(4-acryloylmorpholines)



Scheme S5 Synthetic protocol used for the preparation of linear pNAM and pyrene-labelled pNAM.

The following general protocol was used to prepare linear poly(4-acryloylmorpholines) (**L1-3**). In an 8 ml vial, PABTC (33.74 mg, 0.14 mmol, 1 equiv.) and NAM (1.013 g, 7.18 mmol, 51 equiv.) were dissolved in dioxane (2.65 ml, $[M]_0$=2 M). 30 µl of DMF was added as an internal standard and a sample was taken for ^{1}H NMR analysis. The reaction mixture was deoxygenated by bubbling nitrogen into the solution for 15 min and the vial was irradiated with blue LED light (20-30 °C) for 3 h. After the reaction was stopped, samples were taken for SEC and ^{1}H NMR analyses. Polymer was isolated by precipitating into diethyl ether three times and drying in a vacuum oven (30 min, 38 °C). The product was characterised with SEC in DMF and ^{1}H NMR in $CDCl_3$.

To prepare pyrene-functional pNAM (**L4**), NAM (100 mg, 0.71 mmol), pyr-PBTC (29.2 mg, $5.9\cdot10^{-2}$ mmol) and ACVA (0.2 mg, $7.08\cdot10^{-4}$ mmol) were dissolved in dioxane (147 µl) in a 1.5 ml screw cap glass vial. The mixture was degassed with nitrogen for 10 min and placed in an oil bath heated to 75 °C for 24 h. Conversion was determined by ^{1}H NMR in $CDCl_3$. The reaction mixture was precipitated twice into ice-cold diethyl ether and dried overnight in a vacuum oven (40 °C).

Table S4 Linear pNAM polymers employed in this work.

	Structure [A]	Conversion [B] %	DP_p [C]	$M_{n,th}$ [E] (g/mol)	$M_{n,SEC}$ [F] (g/mol)	$Đ$ [F]
L1	$pNAM_{20}$	65	20	3,100	2,900	1.12
L2	$pNAM_{30}$	80	30	4,500	4,500	1.12
L3	$pNAM_{44}$	87	44	6,500	6,100	1.10
L4	pyr-$pNAM_{15}$	95	15	2,600	2,700	1.21

[A] The degree of polymerisation was calculated based on conversion as given by ^{1}H NMR ($CDCl_3$).
[B] Determined by ^{1}H NMR.
[C] Theoretical average degree of polymerisation as given by conversion.
[D] Extent of functionalisation as given by ^{1}H NMR.
[E] Theoretical number-average molar mass as given by conversion.
[F] Experimental number-average molar mass and dispersity as given by SEC analysis in DMF (**L1**-**3**) or $CHCl_3$ (**L4**) with DRI detection and PMMA calibration.

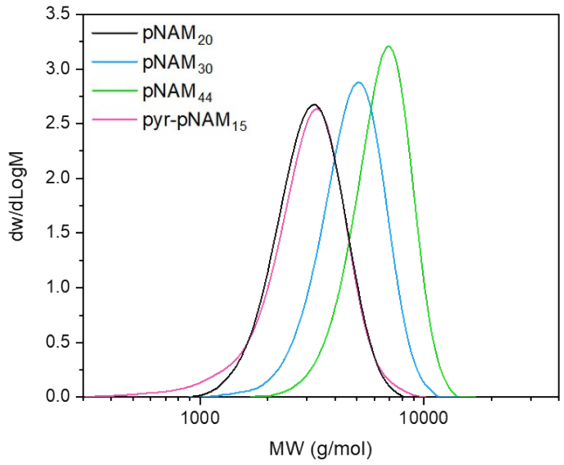
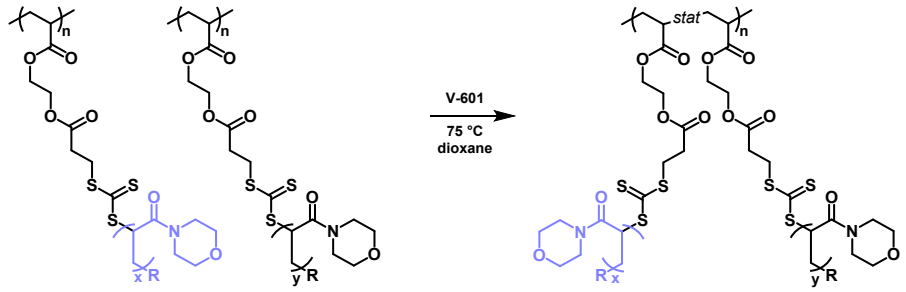


Figure S9 Size exclusion chromatograms of linear pNAM polymers. Analysis was carried out in $CHCl_3$ (pyr-$pNAM_{15}$) or DMF (all other samples) with DRI detection and PMMA calibration.

3.6 Graft exchange using a thermal initiator



Scheme S6 Synthetic approach used for graft exchange reactions with a thermal initiator.

The following general protocol was used for all reactions. For exchanging short and long pNAM grafts at an equimolar ratio, pHEA$_{23}$-*graft*-pNAM$_{10}$ (12.61 mg, $3.1 \cdot 10^{-4}$ mmol) and pHEA$_{23}$-*graft*-pNAM$_{87}$ (12.58 mg, $4.4 \cdot 10^{-5}$ mmol) were weighed into a 2 ml screw-cap septum vial. Dioxane (0.40 ml) and initiator stock solution (0.90 mg/ml in dioxane, $[CTA]/[I]_0 = 20$) were added to dissolve the polymers and the solution was purged with nitrogen for 10 min. The vial was placed in a pre-heated oil bath set at 75 °C. Samples were withdrawn for SEC analysis through the septum with a nitrogen-flushed syringe.

Table S5 SEC analysis results for graft exchange reactions carried out using a thermal initiator. Mass of terminated chains (m_T) was quantified from RI vs. RT data.

ID	Polymers used in the reaction	Mixing ratio	Before exchange		After exchange		
			$M_{n,SEC}$ [A] (g/mol)	$Đ$ [A]	$M_{n,SEC}$ [A] (g/mol)	$Đ$ [A]	m_T (%)
E1	pHEA$_{23}$-*graft*-pNAM$_{10}$ pHEA$_{23}$-*graft*-pNAM$_{87}$	1:1 mass	28,000 169,000	1.14 1.51	39,600	1.46	4
E2	pHEA$_{23}$-*graft*-pNAM$_{10}$ pHEA$_{300}$-*graft*-pNAM$_{51}$	1:1 mol grafts	28,000 480,000	1.14 1.42	N/A[B]	N/A[B]	12

[A] Experimental number-average molar mass and dispersity as given by SEC analysis in $CHCl_3$ with dRI detection and PMMA calibration.
[B] Not quantified, see Figure S7.

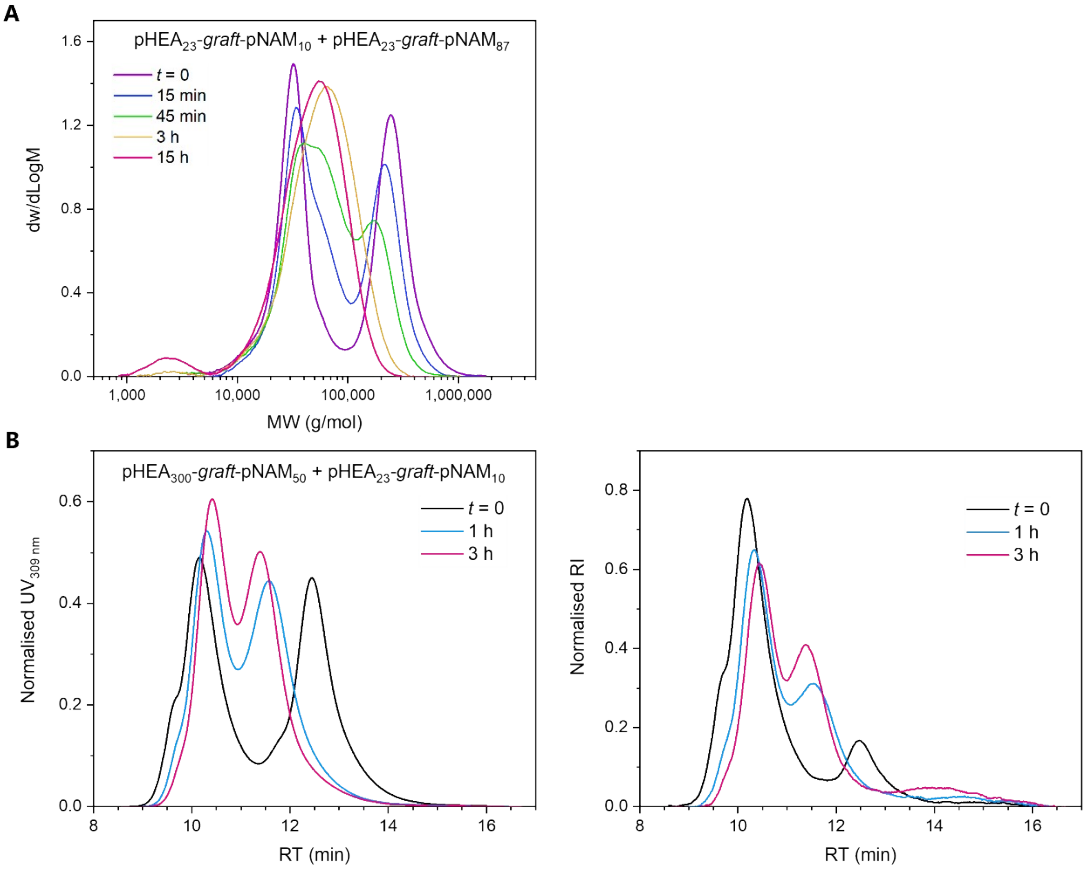


Figure S10 Size exclusion chromatograms of graft exchange reactions between bottlebrush polymers with equal backbone lengths but distinct graft lengths, $pHEA_{23}$-*graft*-$pNAM_{10}$ and $pHEA_{23}$-*graft*-$pNAM_{87}$ (**A**), and bottlebrush polymers with both distinct backbone and graft lengths, $pHEA_{300}$-*graft*-$pNAM_{50}$ and $pHEA_{23}$-*graft*-$pNAM_{10}$ (**B**). Analyses were carried out in DMF with DRI detection and PMMA calibration.

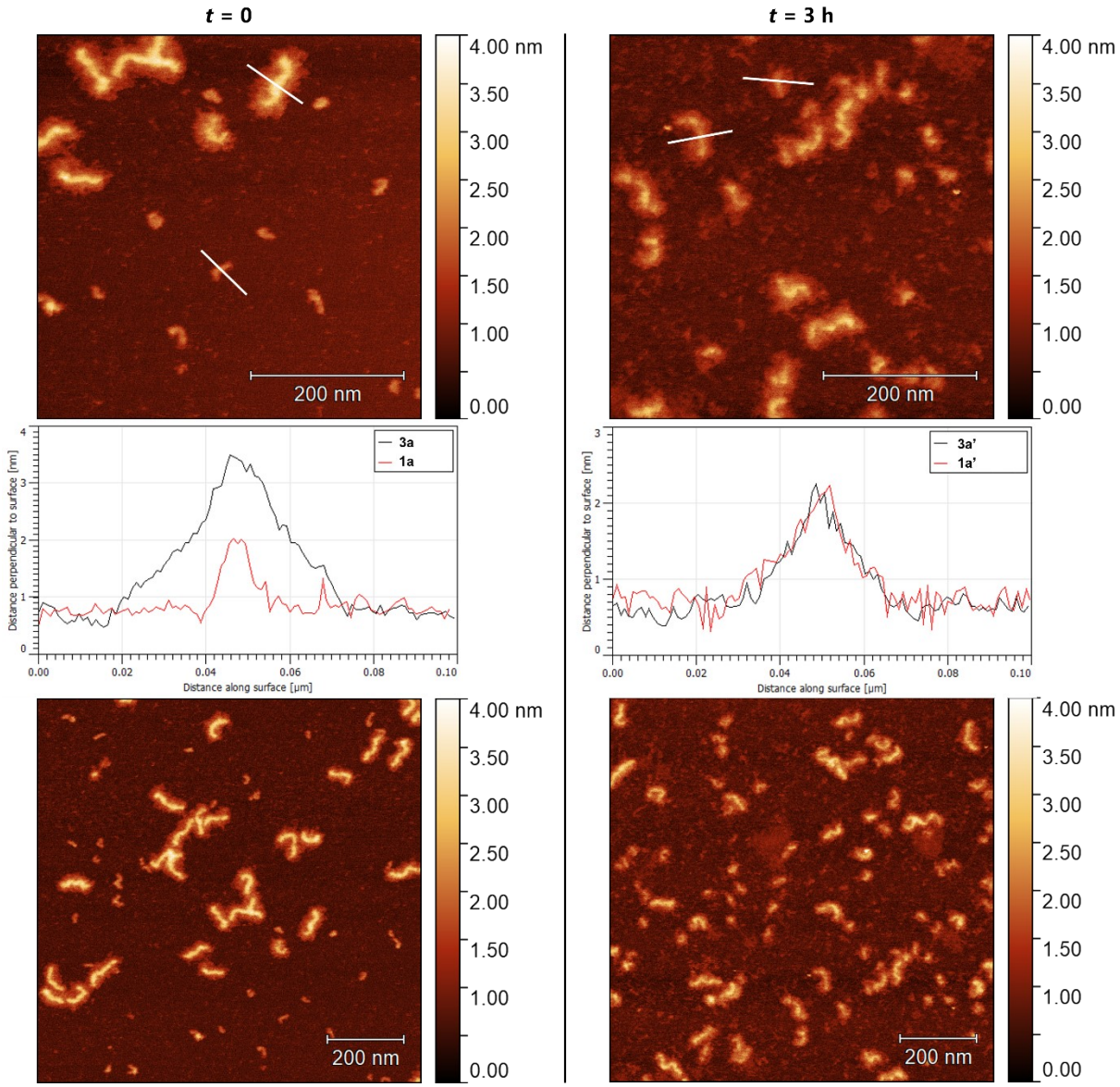
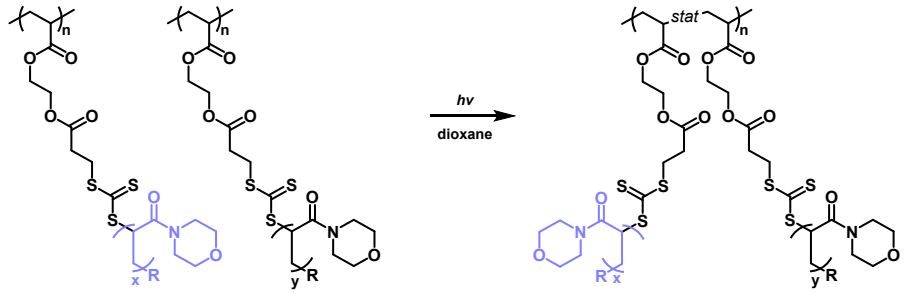


Figure S11 AFM images and height profiles of an equimolar mixture of $pHEA_{23}$-*graft*-$pNAM_{10}$ (**1a**) and $pHEA_{300}$-*graft*-$pNAM_{51}$ (**3a**) bottlebrush polymers on mica before (t = 0) and after exchange (t = 3 h).

3.7 Graft exchange using the photoiniferter approach



Scheme S7. Synthetic approach used for photoiniferter graft exchange reactions.

The following general protocol was used for all reactions. For exchanging short and long pNAM side chains at an equal mass ratio, pHEA$_{23}$-*graft*-pNAM$_{10}$ (10.02 mg, $2.4 \cdot 10^{-4}$ mmol) and pHEA$_{23}$-*graft*-pNAM$_{87}$ (10.05 mg, $3.5 \cdot 10^{-4}$ mmol) were weighed into a 2 ml screw-cap septum vial. Dioxane (0.40 ml) was added to dissolve the polymers. The solution was purged with nitrogen for 10 min and the vial was placed in a photoreactor equipped with blue LED light strips (30-40 °C). Samples were taken for GPC analysis through the septum with a nitrogen-flushed syringe.

Table S6 SEC analysis results for graft exchange reactions carried out using the photoiniferter approach. Mass of terminated chains (m_T) was quantified from RI vs. RT data.

ID	Polymers used in the reaction	Mass ratio	Before exchange $M_{n,SEC}$ [A] (g/mol)	Before exchange $Đ$ [A]	After exchange $M_{n,SEC}$ [A] (g/mol)	After exchange $Đ$ [A]	m_T (%)
E3	pHEA$_{23}$-*graft*-pNAM$_{10}$ pHEA$_{23}$-*graft*-pNAM$_{87}$	1:1	28,000 169,000	1.14 1.51	42,400	1.48	6
E4.1	pHEA$_{133}$-*graft*-pNAM$_{8}$ pHEA$_{133}$-*graft*-pNAM$_{29}$	1:1	56,700 157,000	1.32 1.34	101,000	1.16	4
E4.2	pHEA$_{133}$-*graft*-pNAM$_{8}$ pHEA$_{133}$-*graft*-pNAM$_{29}$	1:2	56,700 157,000	1.32 1.34	121,000	1.13	7
E4.3	pHEA$_{133}$-*graft*-pNAM$_{8}$ pHEA$_{133}$-*graft*-pNAM$_{29}$	2:1	56,700 157,000	1.32 1.34	88,200	1.16	N/A[B]

[A] Experimental number-average molar mass and dispersity as given by SEC analysis in DMF with DRI detection and PMMA calibration.
[B] Below the detection limit.

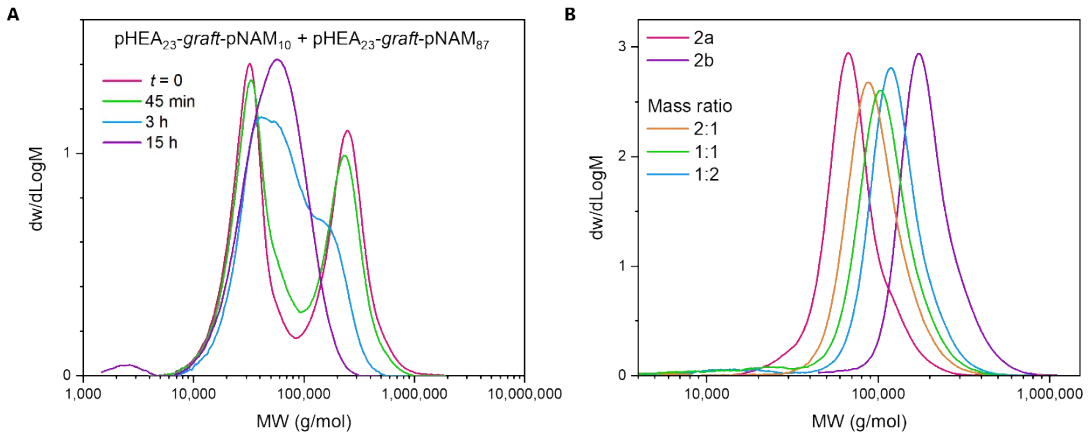
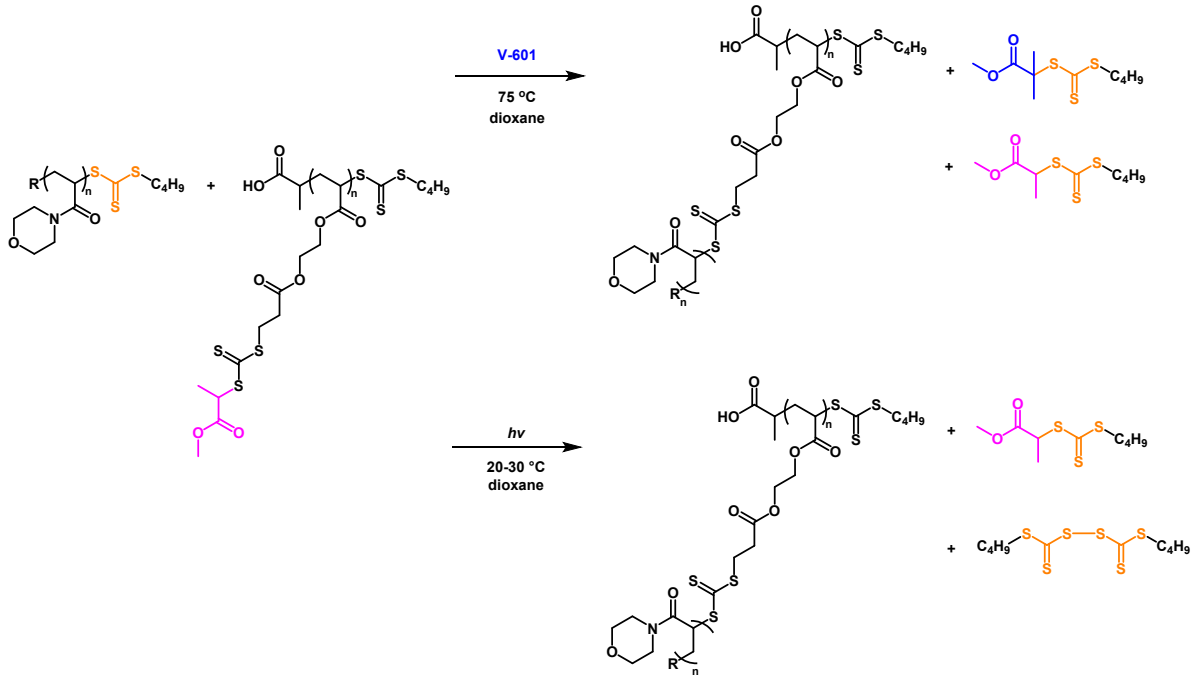


Figure S12. Size exclusion chromatograms of photoiniferter graft exchange reactions between pHEA$_{23}$-*graft*-pNAM$_{10}$ (**1a**) and pHEA$_{23}$-*graft*-pNAM$_{87}$ (**1b**) at an equal mass ratio (**A**), and pHEA$_{133}$-*graft*-pNAM$_{8}$ (**2a**) and pHEA$_{133}$-*graft*-pNAM$_{29}$ (**2b**) at a 1:1, 1:2, and 2:1 mass ratio (**B**). Analyses were carried out in DMF with DRI detection and PMMA calibration.

3.8 Transfer of linear polymer onto polyCTAs



Scheme S8 Transfer-to reaction between linear pNAM and CTA-functionalised backbone with a thermal initiator (top) or in the absence of initiator using blue LED-light (bottom). Two UV-active by-products may be expected to form in each case.

The following general protocol was used for all reactions. For transferring $pNAM_{44}$ side chains to $pCTA_{300}$ at an equimolar ratio of linear polymer to $pCTA_{300}$ repeat unit, $pCTA_{300}$ (1.49 mg, $1.4 \cdot 10^{-8}$ mol, 1 equiv. with respect to MPPATC units) and $pNAM_{44}$ (25.22 mg, $3.9 \cdot 10^{-6}$ mol, 1 equiv.) were weighed into a 2 ml screw-cap septum vial. Dioxane (c_{tot}=50 mg/ml) was added to dissolve the polymers. For reactions employing a thermal initiator, V-601 ($[MPPATC]/[I]_0 = 20$) was added. The solution was purged with nitrogen for 10 min and the vial was either immersed in a pre-heated oil bath set at 75 °C for 4 h or placed under blue LED light. Reaction was monitored by sampling through the septum with a nitrogen-purged needle. SEC analysis was carried out in DMF.

The transfer efficiencies were calculated from the areas under the SEC $UV_{\lambda=309nm}$ detector responses arising from the $pCTA_{300}$ (A_{pCTA}), linear polymer (A_{Lin}), CTA-derived by-product (A_{CTA}), and the graft copolymer (A_{BB}). The linear polymer to backbone CTA ratio was calculated as

$$R = \frac{A_{Lin}}{A_{pCTA}}. \qquad (S5)$$

The fraction of linear chains consumed in the reaction was estimated as

$$f_{Lin,UV} = \frac{A_{CTA}}{A_{CTA+Lin}}. \qquad (S6)$$

The relative transfer efficiency, related to the grafting density, was calculated by taking into account the initial ratio of linear chains to backbone CTA as

$$f_{Rel,UV} = R\, f_{Lin,UV}. \qquad (S7)$$

The transfer efficiencies could also be estimated using the DRI detector response when the signal-to-noise ratio was sufficiently large. When a large excess of linear chains was used, a small deviation in A_{pCTA} could result in a significant error in the result. The mass fraction of linear chains at time t was calculated as

$$\%\ Lin_t = \frac{A_{Lin,t}}{A_{tot,t}}, \qquad (S8)$$

where $A_{tot,t}$ is the sum of all areas at time t. The change in the mass fraction of linear chains by time t was then

$$\Delta\ Lin_t = \frac{A_{Lin,t}}{A_{Lin,0}}, \qquad (S9)$$

where $A_{Lin,0}$ is the mass fraction at $t = 0$. The fraction of linear chains consumed after time t was then calculated as

$$f_{Lin,RI} = \frac{\Delta Lin_t}{\%\ Lin_t} \qquad (S10)$$

and the relative transfer efficiency as

$$f_{Rel,RI} = R\, f_{Lin,RI}\,. \qquad (S11)$$

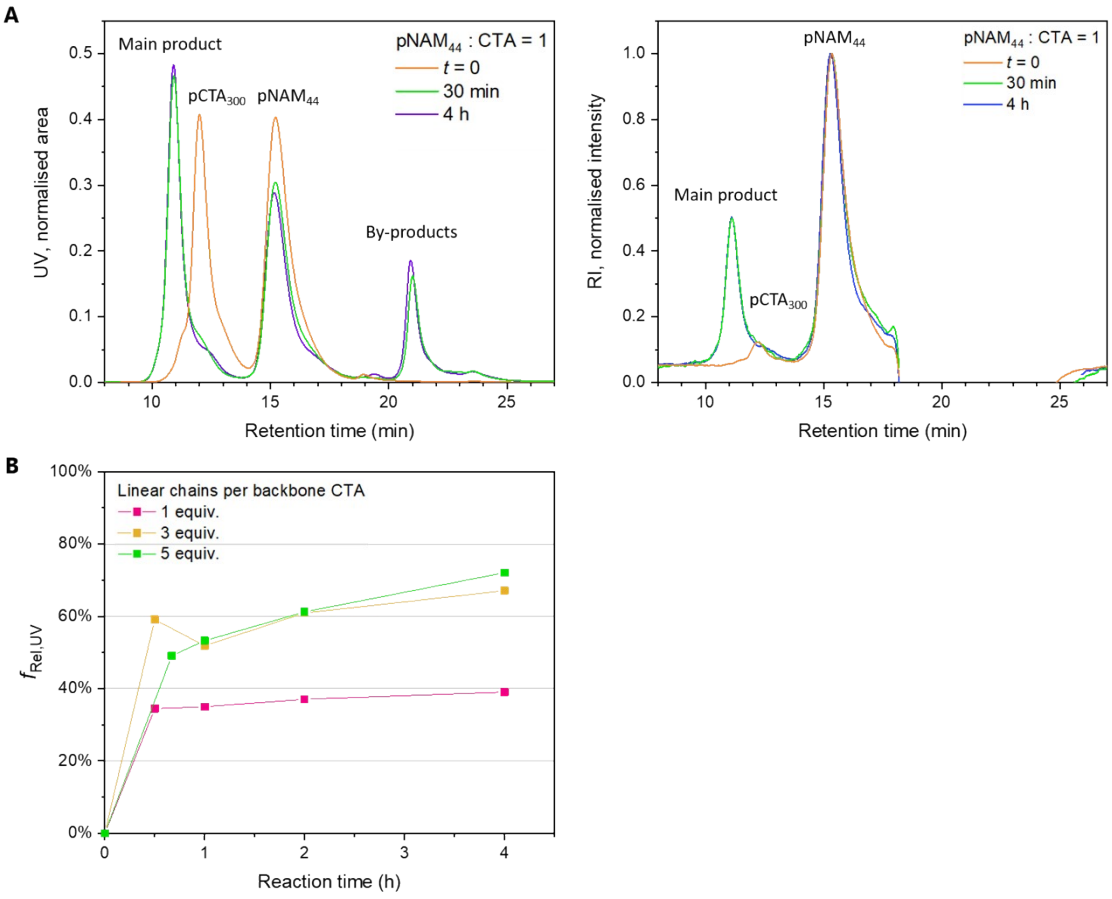
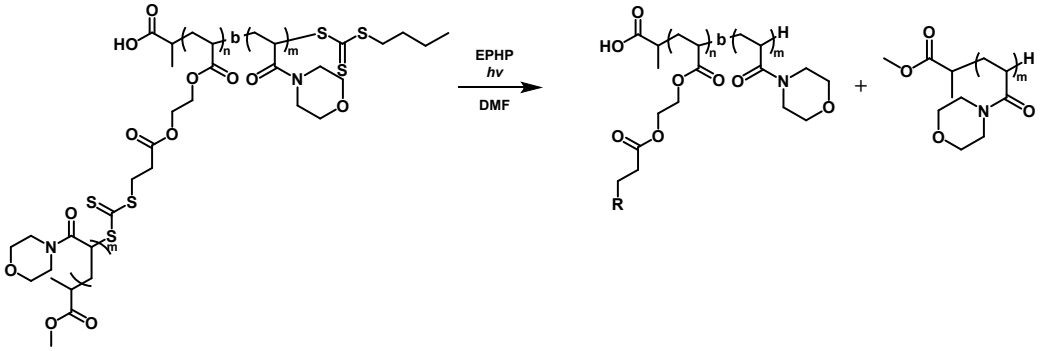


Figure S13 A) Size exclusion chromatograms of three time points taken during $pNAM_{44}$ transfer to $pCTA_{300}$ with an added initiator. Data was collected in DMF. **B**) Relative fraction of transferred linear chains, descriptive of the grafting density, calculated from UV data using Eq. S7.

Table S7 Characterisation details for reactions between linear pNAM and $pCTA_{300}$. Size exclusion chromatography with DRI and $UV_{\lambda=309nm}$ detectors was used to follow reaction kinetics. The extent of linear transfer was quantified by plotting the raw data and comparing the areas under the peaks corresponding to linear chains, $pCTA_{300}$/graft copolymer, and the CTA-derived UV-active by-product. Relative fractions of transferred linear chains (f_{Rel}), descriptive of grafting density, were calculated using Eq. S7 and S11.

	Initiation	DP of pNAM	[pNAM]/[CTA] (mol)	Reaction time (h)	RI detection % Transferred	RI detection f_{Rel}	UV detection % Transferred	UV detection f_{Rel}
T1	Δ	44	1:1	4	24	31	31	39
T2	Δ	44	3:1	4	13	35	24	67
T3	Δ	44	5:1	4	0	2	15	72
T4	*hv*	20	1:1	1.5	28	35	31	40
T5	*hv*	30	1:1	1.5	25	31	31	38
T6	*hv*	44	1:1	1.5	23	28	27	34

3.9 Cleaving grafts off bottlebrush backbones



Scheme S9. Synthetic approach used to cleave grafts off backbone to study their dispersity with size-exclusion chromatography.

Grafts were cleaved off the backbones by using blue light-induced fragmentation in the presence of EPHP[3] with the following general protocol. To cleave the grafts of $pHEA_{300}$-*graft*-$pNAM_{35}$, the bottlebrush polymer (10.32 mg, $1.9 \cdot 10^{-3}$ mmol CTA, 1 equiv.) was dissolved with EPHP (5.2 mg, $2.9 \cdot 10^{-2}$ mmol, 15 equiv.) in DMF (0.20 ml). The solution was deoxygenated for 10 min and the vial was irradiated with blue LED light (20-30 °C) for 12 h. The product was analysed by DMF SEC without isolation.

Table S8 Experimental molecular weights ($M_{n,SEC}$) and dispersities ($Đ$) found in the graft cleavage reactions. Analysis was carried out in DMF with DRI detection and PMMA calibration. Notation $pHEA_n$-*graft*-$pNAM_{m(x\%)}$ expresses the relative transfer efficiency (Eq. S11), related to grafting density, as *x*%.

		Bottlebrush		Linear polymer		Cleaved grafts	
		$M_{n,SEC}$ (g/mol)	$Đ$	$M_{n,SEC}$ (g/mol)	$Đ$	$M_{n,SEC}$ (g/mol)	$Đ$
	Linear chain transfer to pCTA						
C-T4	$pHEA_{300}$-*graft*-$pNAM_{20(35\%)}$	138,000	1.17	2,900	1.12	2,850	1.22
C-T5	$pHEA_{300}$-*graft*-$pNAM_{30(31\%)}$	148,000	1.29	4,500	1.12	4,150	1.24
C-T6	$pHEA_{300}$-*graft*-$pNAM_{40(28\%)}$	182,000	1.22	6,100	1.10	5,930	1.18
	Z group approach						
C-3b	$pHEA_{300}$-*graft*-$pNAM_{35}$	368,000	1.51	-	-	7,700	1.74
C-3a	$pHEA_{300}$-*graft*-$pNAM_{50}$	548,000	1.43	-	-	10,400	1.98
C-1b	$pHEA_{23}$-*graft*-$pNAM_{87}$	178,000	1.56	-	-	17,500	1.79
C-2b	$pHEA_{133}$-*graft*-$pNAM_{29}$	157,000	1.34	-	-	6,900	1.58

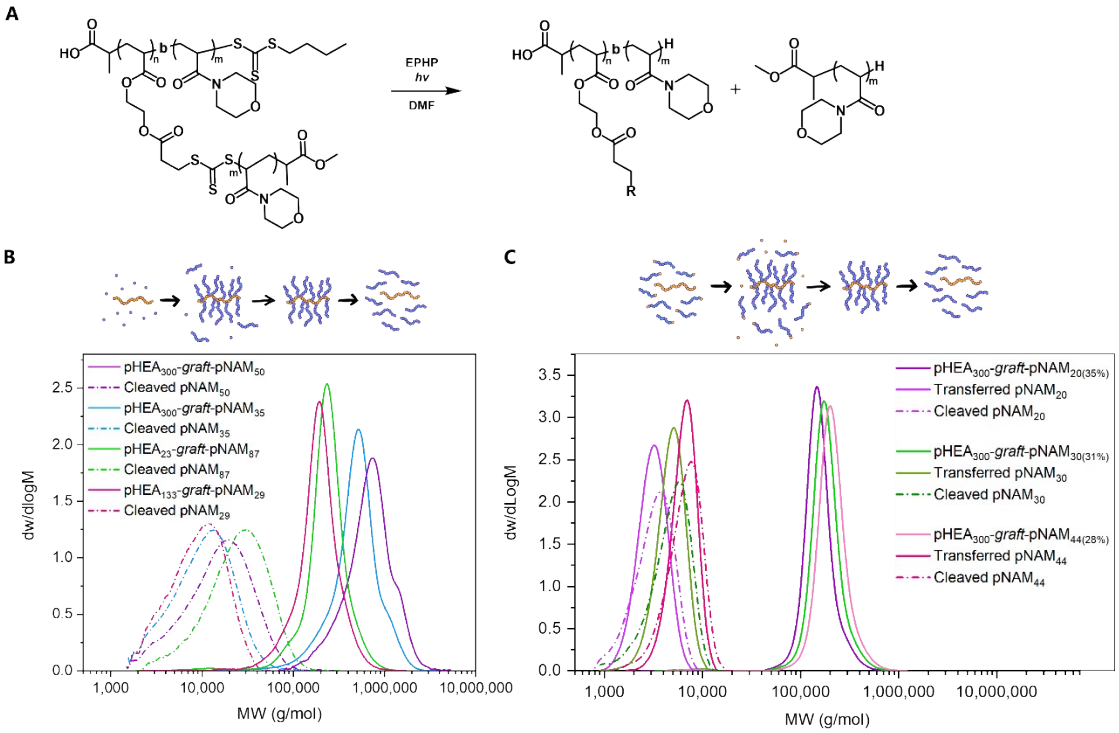


Figure S14 Graft dispersity comparison between graft copolymers prepared through the Z group approach (**A**) and by transferring linear polymers onto functionalised backbones (**B**). Size exclusion chromatography was carried out in DMF with DRI detection and PMMA calibration. Notation $pHEA_n$-*graft*-$pNAM_{m(x\%)}$ expresses the relative transfer efficiency (Eq. S11), related to grafting density, as *x*%.

4 References

1. Larnaudie, S. C.; Brendel, J. C.; Jolliffe, K. A.; Perrier, S., Cyclic peptide–polymer conjugates: Grafting-to vs grafting-from. *Journal of Polymer Science Part A: Polymer Chemistry* **2016,** *54* (7), 1003-1011.
2. Adams, R.; Weeks, L. F., Action of oxalyl chloride on primary, secondary and tertiary alcohols. *Journal of the American Chemical Society* **1916,** *38* (11), 2514-2519.
3. Carmean, R. N.; Figg, C. A.; Scheutz, G. M.; Kubo, T.; Sumerlin, B. S., Catalyst-Free Photoinduced End-Group Removal of Thiocarbonylthio Functionality. *ACS Macro Letters* **2017,** *6* (2), 185-189.