Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

Preparation of Complex Multiblock Copolymers *via* Aqueous RAFT at Room Temperature

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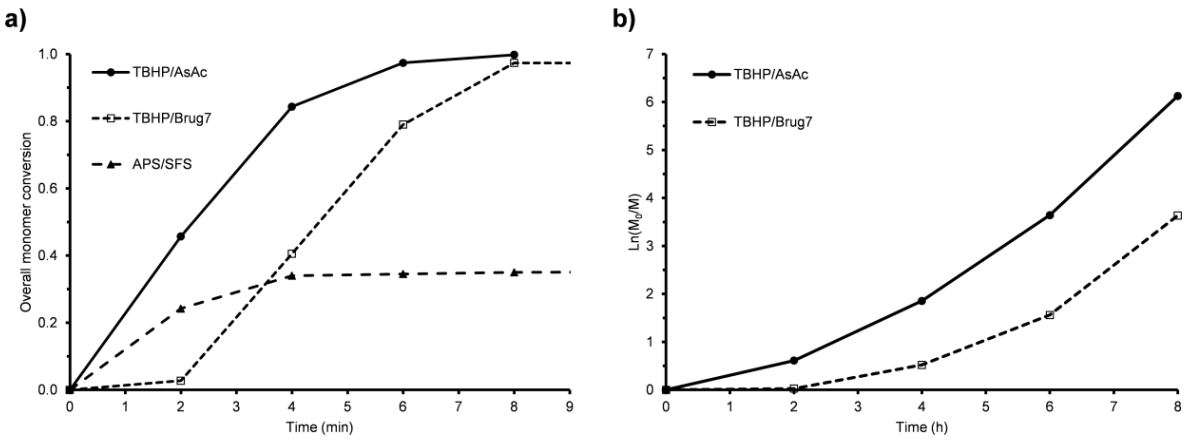


Figure S1 - a) Monomer conversion *vs* time and b) $\ln(M_0/M)$ *vs* time for RAFT of $PNAM_{10}$ in H_2O/dioxane at 25 °C using different redox pairs as initiator. $[NAM]_0$ = 3 M, $[Ox]_0 = [Red]_0 = 3.0\ 10^{-3}$ M, H_2O:dioxane 70:30 (v:v), where $[Ox]_0$ is the initial concentration of the oxidizing agent (TBHP or APS) and $[Red]_0$ is the initial concentration of the reducing agent (AsAc, Brug7 or SFS).

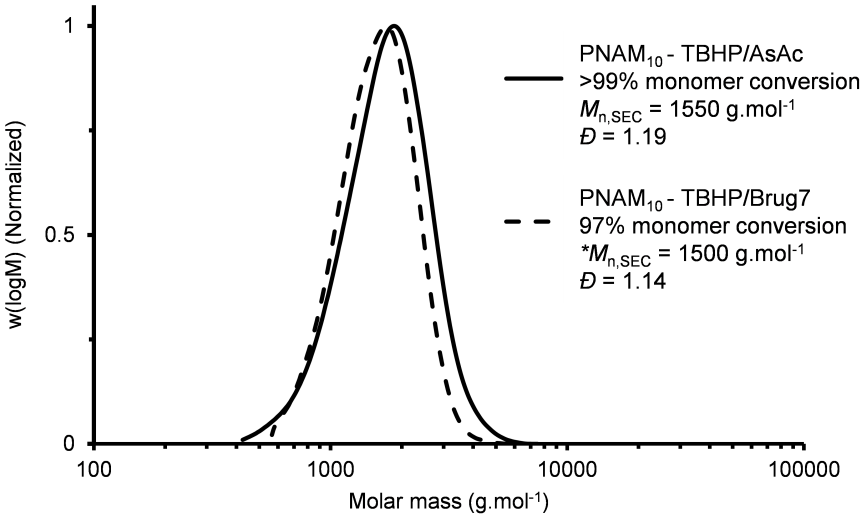


Figure S2 - DMF-SEC analysis of $PNAM_{10}$ prepared after 24 h of RAFT in H_2O/dioxane at 25 °C using TBHP/AsAc (solid line) and TBHP/Brug7 (dashed line) as redox initiator. $[NAM]_0$ = 3.0 M, $[TBHP]_0 = [Red]_0 = 3.0\ 10^{-3}$ M, H_2O:dioxane 70:30 (v:v), where $[Red]_0$ is the initial concentration of the reducing agent (AsAc or Brug7). * sample partially elutes with system peak at low molar mass.

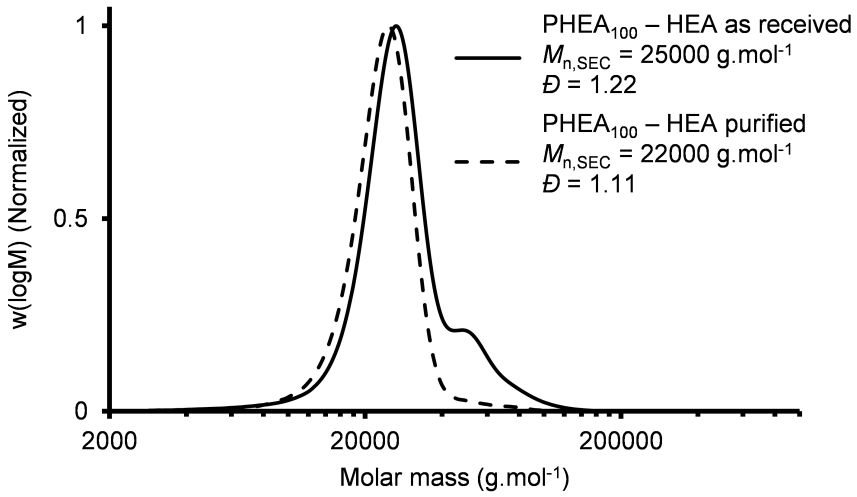


Figure S3 - DMF-SEC of $PHEA_{100}$ prepared *via* RAFT in H_2O/dioxane at 25 °C using TBHP/AsAc redox pair as initiator using HEA as received from Sigma Aldrich (solid line) and purified HEA (dashed line) $[HEA]_0$ = 3.0 M, $[TBHP]_0$ = 3.0 10^{-3} M, $[TBHP]_0$:$[AsAc]_0$ 1:0.5, $[PABTC]_0/[TBHP]_0$ = 7.

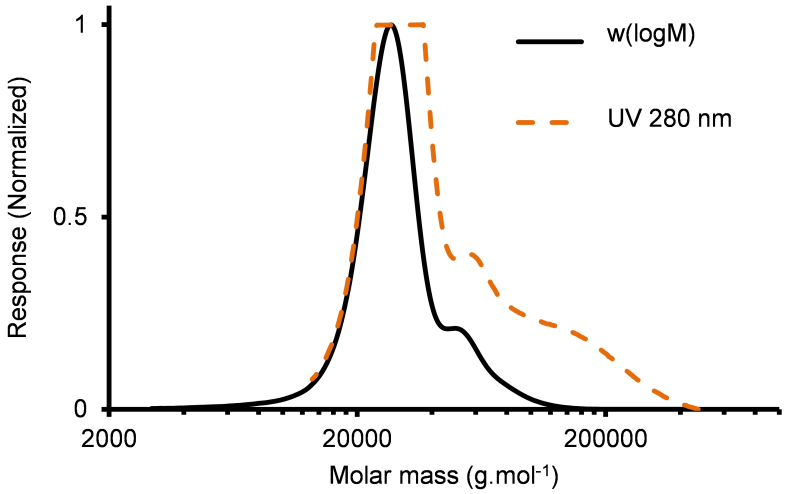
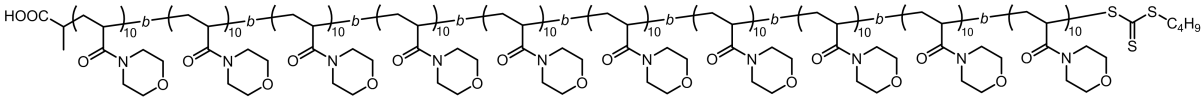
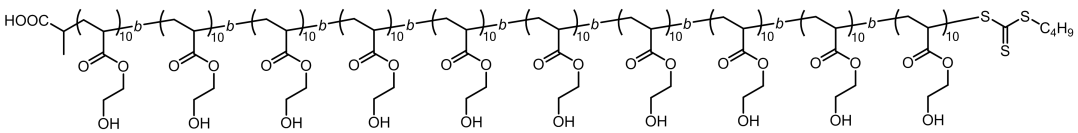


Figure S4 - DMF-SEC analysis of $PHEA_{100}$ prepared *via* RAFT in H_2O/dioxane at 25 °C using TBHP/AsAc redox pair as initiator using HEA as received from Sigma Aldrich. $[HEA]_0$ = 3.0 M, $[TBHP]_0$ = 3.0 10^{-3} M, $[TBHP]_0$:$[AsAc]_0$ 1:0.5, $[PABTC]_0/[TBHP]_0$ = 7.



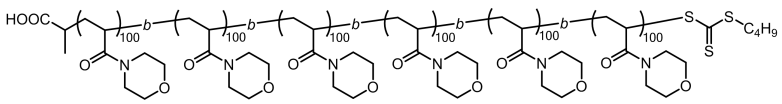
a) Decablock homopolymer:

$PNAM_{10}$-*b*-$PNAM_{10}$-*b*-$PNAM_{10}$-*b*-$PNAM_{10}$-*b*-$PNAM_{10}$-*b*-$PNAM_{10}$-*b*-$PNAM_{10}$-*b*-$PNAM_{10}$-*b*-$PNAM_{10}$-*b*-$PNAM_{10}$



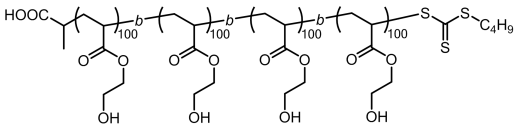
b) Decablock homopolymer:

$PHEA_{10}$-*b*-$PHEA_{10}$-*b*-$PHEA_{10}$-*b*-$PHEA_{10}$-*b*-$PHEA_{10}$-*b*-$PHEA_{10}$-*b*-$PHEA_{10}$-*b*-$PHEA_{10}$-*b*-$PHEA_{10}$-*b*-$PHEA_{10}$



c) Hexablock homopolymer:

$PNAM_{100}$-*b*-$PNAM_{100}$-*b*-$PNAM_{100}$-*b*-$PNAM_{100}$-*b*-$PNAM_{100}$-*b*-$PNAM_{100}$



d) Tetrablock homopolymer:

$PHEA_{100}$-*b*-$PHEA_{100}$-*b*-$PHEA_{100}$-*b*-$PHEA_{100}$-*b*-$PHEA_{100}$

Scheme S1 – Microstructures of multiblock homopolymers prepared in this work

Table S1 - Conditions used in preparation of $(PNAM_{10})_{10}$ *via* RAFT in H_2O/dioxane at 25 °C using TBHP/AsAc redox pair as initiator.

Block	1	2	3	4	5	6	7	8	9	10
Monomer	NAM	NAM	NAM	NAM	NAM	NAM	NAM	NAM	NAM	NAM
$DP_{targeted}$	10	10	10	10	10	10	10	10	10	10
$m_{monomer\ added}$ (mg)	400.0	400.0	400.0	400.0	400.0	400.0	400.0	400.0	400.0	400.0
$m_{CTA\ added}$ (mg)	67.6	-	-	-	-	-	-	-	-	-
$m_{TBHP\ added}$ (mg)	0.51	0.17	0.26	0.32	0.43	0.51	0.64	0.73	0.75	0.75
$m_{AsAc\ added}$ (mg)	0.50	0.17	0.25	0.31	0.42	0.50	0.62	0.71	0.73	0.73
$V_{H2O\ added}$ (mL)	0.412	0.588	0.588	0.588	0.588	0.588	0.588	0.453	0.453	0.453
$V_{dioxane\ added}$ (mL)	0.176	-	-	-	-	-	-	-	-	-
% H_2O	70.1	85.0	90.0	92.5	94.0	95.0	95.7	96.1	96.5	96.8
V_{total} (mL)[a]	0.945	1.889	2.883	3.778	4.722	5.667	6.611	7.421	8.231	9.040
$[Mon]_0$ ($mol.L^{-1}$)[b]	3.00	1.50	1.00	0.75	0.60	0.50	0.43	0.38	0.34	0.31
$[TBHP]_0$ ($mol.L^{-1}$)[c]	$6.00\ 10^{-3}$	$1.00\ 10^{-3}$	$1.00\ 10^{-3}$	$9.38\ 10^{-4}$	$1.00\ 10^{-3}$	$1.00\ 10^{-3}$	$1.07\ 10^{-3}$	$1.09\ 10^{-3}$	$1.01\ 10^{-3}$	$9.22\ 10^{-4}$
$[AsAc]_0$ ($mol.L^{-1}$)[c]	$3.00\ 10^{-3}$	$5.00\ 10^{-4}$	$5.00\ 10^{-4}$	$4.69\ 10^{-4}$	$5.00\ 10^{-4}$	$5.00\ 10^{-4}$	$5.36\ 10^{-4}$	$5.46\ 10^{-4}$	$5.07\ 10^{-4}$	$4.61\ 10^{-4}$
$[PABTC]_0/[TBHP]_0$[d]	50	150	100	80	60	50	40	35	34	34

[a] Represents the sum of the volume of the monomer added + volume of solvent + V_{total} from the previous block. [b] Represents the concentration of the monomer at the beginning of each block extension. [c] The concentration of TBHP/AsAc at the beginning of each block, assuming full consumption of both TBHP and AsAc in the previous block. [d] The theoretical ratio of PABTC chain transfer agent to TBHP oxidant, assuming full consumption of TBHP in previous block.

Table S2 - Monomer conversion and THF-SEC analysis of $(PNAM_{10})_{10}$ prepared *via* RAFT in H_2O/dioxane at 25 °C using TBHP/AsAc redox pair as initiator.

Block	Multiblock poly(4-acryloylmorpholine) composition	Overall monomer conversion (%)[a]	$M_{n,th}$ ($g.mol^{-1}$)[b]	$M_{n,SEC}$ ($g.mol^{-1}$)[c]	$Đ$[c]
1	$PNAM_{10}$	>99	1600	1000	1.17
2	$PNAM_{10}$-*b*-$PNAM_{10}$	>99	3000	1700	1.15
3	$PNAM_{10}$-*b*-$PNAM_{10}$-*b*-$PNAM_{10}$	>99	4400	2500	1.16
4	$PNAM_{10}$-*b*-$PNAM_{10}$-*b*-$PNAM_{10}$-*b*-$PNAM_{10}$	96.5	5800	3500	1.18
5	$PNAM_{10}$-*b*-$PNAM_{10}$-*b*-$PNAM_{10}$-*b*-$PNAM_{10}$-*b*-$PNAM_{10}$	>99	7200	4400	1.16
6	$PNAM_{10}$-*b*-$PNAM_{10}$-*b*-$PNAM_{10}$-*b*-$PNAM_{10}$-*b*-$PNAM_{10}$-*b*-$PNAM_{10}$	>99	8600	5400	1.18
7	$PNAM_{10}$-*b*-$PNAM_{10}$-*b*-$PNAM_{10}$-*b*-$PNAM_{10}$-*b*-$PNAM_{10}$-*b*-$PNAM_{10}$-*b*-$PNAM_{10}$	>99	10000	6600	1.19
8	$PNAM_{10}$-*b*-$PNAM_{10}$-*b*-$PNAM_{10}$-*b*-$PNAM_{10}$-*b*-$PNAM_{10}$-*b*-$PNAM_{10}$-*b*-$PNAM_{10}$-*b*-$PNAM_{10}$	>99	11400	7500	1.21
9	$PNAM_{10}$-*b*-$PNAM_{10}$-*b*-$PNAM_{10}$-*b*-$PNAM_{10}$-*b*-$PNAM_{10}$-*b*-$PNAM_{10}$-*b*-$PNAM_{10}$-*b*-$PNAM_{10}$-*b*-$PNAM_{10}$	>99	12900	9000	1.17
10	$PNAM_{10}$-*b*-$PNAM_{10}$-*b*-$PNAM_{10}$-*b*-$PNAM_{10}$-*b*-$PNAM_{10}$-*b*-$PNAM_{10}$-*b*-$PNAM_{10}$-*b*-$PNAM_{10}$-*b*-$PNAM_{10}$-*b*-$PNAM_{10}$	>99	14300	10100	1.19

[a] Determined by ^1H NMR using eq. 1. [b] Determined using eq. 2.[c] Determined using THF-SEC

Table S3 - Conditions used in preparation of $(PNAM_{10})_{10}$ *via* RAFT in H_2O/dioxane at 70 °C using VA-044 as thermal azoinitiator.

Block	1	2	3	4	5	6	7	8	9	10
Monomer	NAM	NAM	NAM	NAM	NAM	NAM	NAM	NAM	NAM	NAM
$DP_{targeted}$	10	10	10	10	10	10	10	10	10	10
$m_{monomer\ added}$ (mg)	400.0	400.0	400.0	400.0	400.0	400.0	400.0	400.0	400.0	400.0
$m_{CTA\ added}$ (mg)	67.6	-	-	-	-	-	-	-	-	-
$m_{VA\text{-}044\ added}$ (mg)	0.23	0.12	0.18	0.25	0.31	0.35	0.40	0.44	0.48	0.54
$V_{H2O\ added}$ (mL)	0.470	0.588	0.588	0.588	0.588	0.352	0.352	0.352	0.352	0.352
$V_{dioxane\ added}$ (mL)	0.118	-	-	-	-	-	-	-	-	-
% H_2O	80.0	90.0	93.3	95.0	96.0	96.4	96.8	97.1	97.3	97.5
V_{total} (mL)[a]	0.994	1.889	2.883	3.778	4.722	5.431	6.139	6.848	7.556	8.265
$m_{VA\text{-}044total}$ (mg)[b]	0.23	0.13	0.19	0.26	0.32	0.37	0.42	0.46	0.51	0.56
$[Mon]_0$ ($mol.L^{-1}$)[c]	3.00	1.50	1.00	0.75	0.60	0.52	0.46	0.41	0.37	0.34
$[VA\text{-}044]_0$ ($mol.L^{-1}$)	$7.50\ 10^{-4}$	$2.17\ 10^{-4}$	$2.07\ 10^{-4}$	$2.11\ 10^{-4}$	$2.08\ 10^{-4}$	$2.10\ 10^{-4}$	$2.10\ 10^{-4}$	$2.06\ 10^{-4}$	$2.07\ 10^{-4}$	$2.11\ 10^{-4}$
$[PABTC]_0/[VA\text{-}044]_0$	400	691	483	356	288	249	220	201	181	162

[a] Represents the sum of the volume of the monomer added + volume of solvent + V_{total} from the previous block. [b] $m_{VA\text{-}044}$ t_{total} represents the sum of the initiator added $m_{VA\text{-}044\ added}$ + the amount of initiator remaining from the previous block . [c] Represents the concentration of the monomer at the beginning of each block extension.

Table S4 - Monomer conversion and THF-SEC analysis of $(PNAM_{10})_{10}$ prepared *via* RAFT in H_2O/dioxane at 70 °C using VA-044 as thermal azoinitiator.

Block	Multiblock poly(4-acryloylmorpholine) composition	Overall monomer conversion (%)[a]	$M_{n,th}$ ($g.mol^{-1}$)[b]	$M_{n,SEC}$ ($g.mol^{-1}$)[c]	$Đ$[c]
1	$PNAM_{10}$	>99	1600	1100	1.13
2	$PNAM_{10}$-*b*-$PNAM_{10}$	>99	3100	2100	1.10
3	$PNAM_{10}$-*b*-$PNAM_{10}$-*b*-$PNAM_{10}$	>99	4500	2900	1.10
4	$PNAM_{10}$-*b*-$PNAM_{10}$-*b*-$PNAM_{10}$-*b*-$PNAM_{10}$	>99	5900	3900	1.10
5	$PNAM_{10}$-*b*-$PNAM_{10}$-*b*-$PNAM_{10}$-*b*-$PNAM_{10}$-*b*-$PNAM_{10}$	>99	7300	4800	1.10
6	$PNAM_{10}$-*b*-$PNAM_{10}$-*b*-$PNAM_{10}$-*b*-$PNAM_{10}$-*b*-$PNAM_{10}$-*b*-$PNAM_{10}$	>99	8700	5900	1.09
7	$PNAM_{10}$-*b*-$PNAM_{10}$-*b*-$PNAM_{10}$-*b*-$PNAM_{10}$-*b*-$PNAM_{10}$-*b*-$PNAM_{10}$-*b*-$PNAM_{10}$	>99	10100	6800	1.11
8	$PNAM_{10}$-*b*-$PNAM_{10}$-*b*-$PNAM_{10}$-*b*-$PNAM_{10}$-*b*-$PNAM_{10}$-*b*-$PNAM_{10}$-*b*-$PNAM_{10}$-*b*-$PNAM_{10}$	>99	11500	7400	1.13
9	$PNAM_{10}$-*b*-$PNAM_{10}$-*b*-$PNAM_{10}$-*b*-$PNAM_{10}$-*b*-$PNAM_{10}$-*b*-$PNAM_{10}$-*b*-$PNAM_{10}$-*b*-$PNAM_{10}$-*b*-$PNAM_{10}$	>99	12900	8300	1.13
10	$PNAM_{10}$-*b*-$PNAM_{10}$-*b*-$PNAM_{10}$-*b*-$PNAM_{10}$-*b*-$PNAM_{10}$-*b*-$PNAM_{10}$-*b*-$PNAM_{10}$-*b*-$PNAM_{10}$-*b*-$PNAM_{10}$-*b*-$PNAM_{10}$	>99	14300	9000	1.15

[a] Determined by ^1H NMR using eq. 1. [b] Determined using eq. 2.[c] Determined using THF-SEC

Table S5 - Conditions used in preparation of $(PHEA_{10})_{10}$ *via* RAFT in H_2O/dioxane at 25 °C using TBHP/AsAc redox pair as initiator.

Block	1	2	3	4	5	6	7	8	9	10
Monomer	HEA	HEA	HEA	HEA	HEA	HEA	HEA	HEA	HEA	HEA
$DP_{targeted}$	10	10	10	10	10	10	10	10	10	10
$m_{monomer\ added}$ (mg)	303.3	303.3	303.3	303.3	303.3	303.3	303.3	303.3	303.3	303.3
$m_{CTA\ added}$ (mg)	62.3	-	-	-	-	-	-	-	-	-
$m_{TBHP\ added}$ (mg)	1.18	0.47	0.59	0.78	0.98	0.94	1.10	1.26	1.41	1.57
$m_{AsAc\ added}$ (mg)	1.16	0.46	0.58	0.77	0.97	0.93	1.08	1.24	1.39	1.55
$V_{H2O\ added}$ (mL)	0.399	0.571	0.571	0.571	0.571	0.571	0.571	0.571	0.571	0.571
$V_{dioxane\ added}$ (mL)	0.171	-	-	-	-	-	-	-	-	-
% H_2O	70.0	85.0	90.0	92.5	94.0	95.0	95.7	96.3	96.7	97.0
V_{total} (mL)[a]	0.871	1.741	2.612	3.483	4.353	5.224	6.095	6.965	7.836	8.707
$[Mon]_0$ (mol.L^{-1})[b]	3.00	1.50	1.00	0.75	0.60	0.50	0.43	0.38	0.33	0.30
$[TBHP]_0$ (mol.L^{-1})[c]	1.50 10^{-2}	3.00 10^{-3}	2.50 10^{-3}	2.50 10^{-3}	2.50 10^{-3}	2.00 10^{-3}	2.50 10^{-3}	2.50 10^{-3}	2.50 10^{-3}	2.50 10^{-3}
$[AsAc]_0$ (mol.L^{-1})[c]	7.50 10^{-3}	1.50 10^{-3}	1.25 10^{-3}	1.25 10^{-3}	1.25 10^{-3}	1.50 10^{-3}	1.25 10^{-3}	1.25 10^{-3}	1.25 10^{-3}	1.25 10^{-3}
$[PABTC]_0/[TBHP]_0$[d]	20	50	40	30	24	25	21	19	17	15

[a] Represents the sum of the volume of the monomer added + volume of solvent + V_{total} from the previous block. [b] Represents the concentration of the monomer at the beginning of each block extension. [c] The concentration of TBHP/AsAc at the beginning of each block, assuming full consumption of both TBHP and AsAc in the previous block. [d] The theoretical ratio of PABTC chain transfer agent to TBHP oxidant, assuming full consumption of TBHP in previous block.

Table S6 - Monomer conversion and DMF-SEC analysis of $(PHEA_{10})_{10}$ prepared *via* RAFT in H_2O/dioxane at 25 °C using TBHP/AsAc redox pair as initiator.

Block	Multiblock poly(2-hydroxyethyl acrylate) composition	Overall monomer conversion (%)[a]	$M_{n,th}$ ($g.mol^{-1}$)[b]	$M_{n,SEC}$ ($g.mol^{-1}$)[c]	$Đ$[c]
1	$PHEA_{10}$	>99	1400	3500	1.21
2	$PHEA_{10}$-*b*-$PHEA_{10}$	>99	2500	6200	1.14
3	$PHEA_{10}$-*b*-$PHEA_{10}$-*b*-$PHEA_{10}$	>99	3700	9200	1.12
4	$PHEA_{10}$-*b*-$PHEA_{10}$-*b*-$PHEA_{10}$-*b*-$PHEA_{10}$	99	4800	12100	1.13
5	$PHEA_{10}$-*b*-$PHEA_{10}$-*b*-$PHEA_{10}$-*b*-$PHEA_{10}$-*b*-$PHEA_{10}$	>99	6000	14400	1.19
6	$PHEA_{10}$-*b*-$PHEA_{10}$-*b*-$PHEA_{10}$-*b*-$PHEA_{10}$-*b*-$PHEA_{10}$-*b*-$PHEA_{10}$	>98	7100	17600	1.22
7	$PHEA_{10}$-*b*-$PHEA_{10}$-*b*-$PHEA_{10}$-*b*-$PHEA_{10}$-*b*-$PHEA_{10}$-*b*-$PHEA_{10}$-*b*-$PHEA_{10}$	>99	8300	19900	1.27
8	$PHEA_{10}$-*b*-$PHEA_{10}$-*b*-$PHEA_{10}$-*b*-$PHEA_{10}$-*b*-$PHEA_{10}$-*b*-$PHEA_{10}$-*b*-$PHEA_{10}$-*b*-$PHEA_{10}$	>99	9400	25100	1.34
9	$PHEA_{10}$-*b*-$PHEA_{10}$-*b*-$PHEA_{10}$-*b*-$PHEA_{10}$-*b*-$PHEA_{10}$-*b*-$PHEA_{10}$-*b*-$PHEA_{10}$-*b*-$PHEA_{10}$-*b*-$PHEA_{10}$	>98	10500	29200	1.25
10	$PHEA_{10}$-*b*-$PHEA_{10}$-*b*-$PHEA_{10}$-*b*-$PHEA_{10}$-*b*-$PHEA_{10}$-*b*-$PHEA_{10}$-*b*-$PHEA_{10}$-*b*-$PHEA_{10}$-*b*-$PHEA_{10}$-*b*-$PHEA_{10}$	>98	11600	32000	1.33

[a] Determined by ^1H NMR using eq. 1. [b] Determined using eq. 2. [c] Determined using DMF-SEC

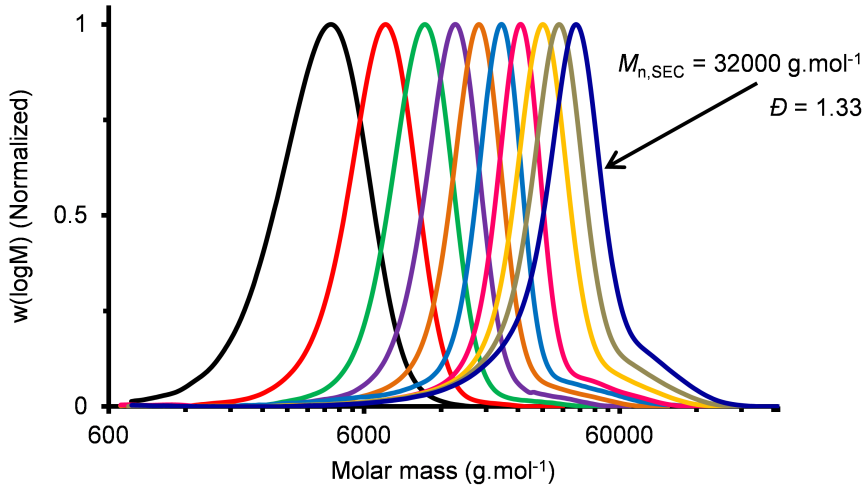


Figure S5 - DMF-SEC chromatograms for $(PHEA_{10})_{10}$ prepared *via* RAFT in H_2O/dioxane at 25 °C using TBHP/AsAc redox pair as initiator.

Table S7 - Conditions used in preparation of $(PHEA_{10})_{10}$ *via* RAFT in H_2O/dioxane at 70 °C using VA-044 as thermal azoinitiator.

Block	1	2	3	4	5	6	7	8	9	10
Monomer	HEA	HEA	HEA	HEA	HEA	HEA	HEA	HEA	HEA	HEA
$DP_{targeted}$	10	10	10	10	10	10	10	10	10	10
$m_{monomer\ added}$ (mg)	303.0	303.0	303.0	303.0	303.0	303.0	303.0	303.0	303.0	303.0
$m_{CTA\ added}$ (mg)	62.2	-	-	-	-	-	-	-	-	-
$m_{VA\text{-}044\ added}$ (mg)	0.84	0.56	0.84	1.12	1.41	1.69	1.97	2.25	2.53	2.81
$V_{H2O\ added}$ (mL)	0.314	0.570	0.570	0.570	0.570	0.570	0.570	0.570	0.570	0.570
$V_{dioxane\ added}$ (mL)	0.171	-	-	-	-	-	-	-	-	-
% H_2O	70.0	85.0	90.0	92.5	94.0	95.0	95.7	96.3	96.7	97.0
V_{total} (mL)[a]	0.870	1.740	2.609	3.479	4.349	5.219	6.089	6.958	7.828	8.698
$m_{VA\text{-}044total}$ (mg)[b]	0.84	0.60	0.87	1.16	1.46	1.76	2.05	2.34	2.64	2.93
$[Mon]_0$ (mol.L^{-1})[c]	3.00	1.50	1.00	0.75	0.60	0.50	0.43	0.38	0.33	0.30
$[VA\text{-}044]_0$ (mol.L^{-1})	2.99 10^{-3}	1.06 10^{-3}	1.03 10^{-3}	1.03 10^{-3}	1.04 10^{-3}	1.04 10^{-3}	1.04 10^{-3}	1.04 10^{-3}	1.04 10^{-3}	1.04 10^{-3}
$[PABTC]_0/[VA\text{-}044]_0$	101	141	97	73	58	48	41	37	32	29

[a] Represents the sum of the volume of the monomer added + volume of solvent + V_{total} from the previous block. [b] $m_{VA\text{-}044}$ t_{otal} represents the sum of the initiator added $m_{VA\text{-}044\ added}$ + the amount of initiator remaining from the previous block . [c] Represents the concentration of the monomer at the beginning of each block extension.

Table S8 - Monomer conversion and DMF-SEC analysis of $(PHEA_{10})_{10}$ prepared *via* RAFT in H_2O/dioxane at 70 °C using VA-044 as thermal azoinitiator.

Block	Multiblock poly(2-hydroxyethyl acrylate) composition	Overall monomer conversion (%)[a]	$M_{n,th}$ ($g.mol^{-1}$)[b]	$M_{n,SEC}$ ($g.mol^{-1}$)[c]	$Đ$[c]
1	$PHEA_{10}$	>99	1400	3400	1.17
2	$PHEA_{10}$-*b*-$PHEA_{10}$	98	2500	6100	1.12
3	$PHEA_{10}$-*b*-$PHEA_{10}$-*b*-$PHEA_{10}$	98	3700	9100	1.10
4	$PHEA_{10}$-*b*-$PHEA_{10}$-*b*-$PHEA_{10}$-*b*-HEA_{10}	98	4800	11200	1.15
5	$PHEA_{10}$-*b*-$PHEA_{10}$-*b*-$PHEA_{10}$-*b*-$PHEA_{10}$-*b*-$PHEA_{10}$	98	5900	13200	1.19
6	$PHEA_{10}$-*b*-$PHEA_{10}$-*b*-$PHEA_{10}$-*b*-$PHEA_{10}$-*b*-$PHEA_{10}$-*b*-HEA_{10}	99	7100	15700	1.24
7	$PHEA_{10}$-*b*-$PHEA_{10}$-*b*-$PHEA_{10}$-*b*-$PHEA_{10}$-*b*-$PHEA_{10}$-*b*-$PHEA_{10}$-*b*-$PHEA_{10}$	97	8100	17500	1.31
8	$PHEA_{10}$-*b*-$PHEA_{10}$-*b*-$PHEA_{10}$-*b*-$PHEA_{10}$-*b*-$PHEA_{10}$-*b*-$PHEA_{10}$-*b*-$PHEA_{10}$-*b*-$PHEA_{10}$	>99	9400	19600	1.37
9	$PHEA_{10}$-*b*-$PHEA_{10}$-*b*-$PHEA_{10}$-*b*-$PHEA_{10}$-*b*-$PHEA_{10}$-*b*-$PHEA_{10}$-*b*-$PHEA_{10}$-*b*-$PHEA_{10}$-*b*-$PHEA_{10}$	>99	10600	23800	1.30
10	$PHEA_{10}$-*b*-$PHEA_{10}$-*b*-$PHEA_{10}$-*b*-$PHEA_{10}$-*b*-$PHEA_{10}$-*b*-$PHEA_{10}$-*b*-$PHEA_{10}$-*b*-$PHEA_{10}$-*b*-$PHEA_{10}$-*b*-$PHEA_{10}$	98	11600	27200	1.36

[a] Determined by ^1H NMR using eq. 1. [b] Determined using eq. 2.[c] Determined using DMF-SEC

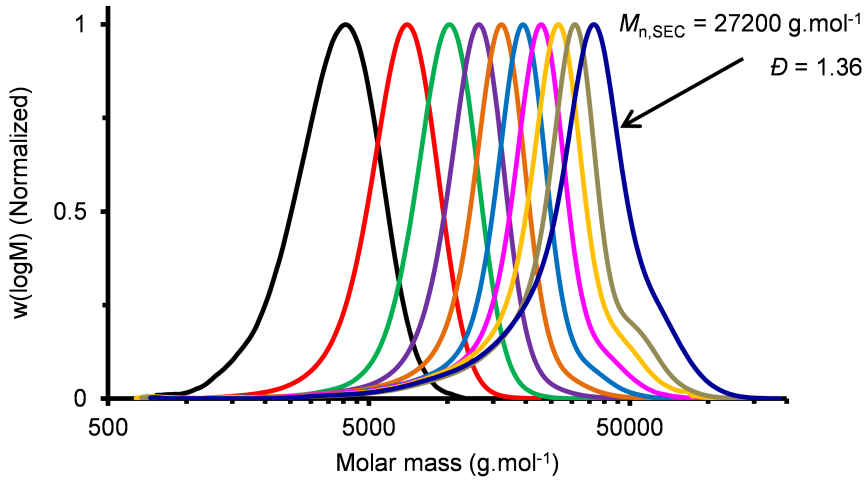


Figure S6 - DMF-SEC chromatograms for $(PHEA_{10})_{10}$ prepared *via* RAFT in H_2O/dioxane at 70 °C using VA-044 as thermal azoinitiator.

Table S9 - Conditions used in preparation of $P(NAM_{100})_6$ *via* RAFT in H_2O/dioxane at 25 °C using TBHP/AsAc redox pair as initiator.

Block	1	2	3	4	5	6
Monomer	NAM	NAM	NAM	NAM	NAM	NAM
$DP_{targeted}$	100	100	100	100	100	100
$m_{monomer\ added}$ (g)	1.00	1.00	1.00	1.00	1.00	1.00
$m_{CTA\ added}$ (mg)	168.9	-	-	-	-	-
$m_{TBHP\ added}$ (mg)	0.21	0.32	0.60	0.85	0.94	1.20
$m_{AsAc\ added}$ (mg)	0.21	0.31	0.58	0.83	0.92	1.18
$V_{H2O\ added}$ (mL)	1.323	1.470	1.470	2.651	1.470	2.651
$V_{dioxane\ added}$ (mL)	0.147	-	-	-	-	-
% H_2O	90.0	95.0	96.7	97.9	98.3	98.7
V_{total} (mL)[a]	2.361	4.722	7.084	10.625	12.987	16.528
$[Mon]_0$ (mol.L^{-1})[b]	3.00	1.50	1.00	0.67	0.55	0.43
$[TBHP]_0$ (mol.L^{-1})[c]	1.00 10^{-3}	7.50 10^{-4}	9.35 10^{-4}	8.89 10^{-4}	8.02 10^{-4}	8.09 10^{-4}
$[AsAc]_0$ (mol.L^{-1})[c]	5.00 10^{-4}	3.75 10^{-4}	4.68 10^{-4}	4.45 10^{-4}	4.01 10^{-4}	4.05 10^{-4}
$[PABTC]_0/[TBHP]_0$[d]	30	20	11	7	7	5

[a] Represents the sum of the volume of the monomer added + volume of solvent + V_{total} from the previous block. [b] Represents the concentration of the monomer at the beginning of each block extension. [c] The concentration of TBHP/AsAc at the beginning of each block, assuming full consumption of both TBHP and AsAc in the previous block. [d] The theoretical ratio of PABTC chain transfer agent to TBHP oxidant, assuming full consumption of TBHP in previous block.

Table S10 - Monomer conversion and DMF-SEC analysis of $(PNAM_{100})_6$ prepared *via* RAFT in H_2O/dioxane at 25 °C using TBHP/AsAc redox pair as initiator.

Block	Multiblock poly(4-acryloylmorpholine) composition	Overall monomer conversion (%)[a]	$M_{n,th}$ ($g.mol^{-1}$)[b]	$M_{n,SEC}$ ($g.mol^{-1}$)[c]	$Đ$[c]
1	$PNAM_{100}$	97	13900	13100	1.07
2	$PNAM_{100}$-*b*-$PNAM_{100}$	>99	28000	37700	1.07
3	$PNAM_{100}$-*b*-$PNAM_{100}$-*b*-$PNAM_{100}$	>99	42200	43700	1.09
4	$PNAM_{100}$-*b*-$PNAM_{100}$-*b*-$PNAM_{100}$-*b*-$PNAM_{100}$	>99	56300	59400	1.13
5	$PNAM_{100}$-*b*-$PNAM_{100}$-*b*-$PNAM_{100}$-*b*-$PNAM_{100}$-*b*-$PNAM_{100}$	>99	70400	73200	1.21
6	$PNAM_{100}$-*b*-$PNAM_{100}$-*b*-$PNAM_{100}$-*b*-$PNAM_{100}$-*b*-$PNAM_{100}$-*b*-$PNAM_{100}$	>99	84500	84700	1.31

[a] Determined by ^1H NMR using eq. 1. [b] Determined using eq. 2. [c] Determined using DMF-SEC

Table S11 - Conditions used in preparation of $(PHEA_{100})_4$ *via* RAFT in H_2O/dioxane at 25 °C using TBHP/AsAc redox pair as initiator.

Block	1	2	3	4
Monomer	HEA	HEA	HEA	HEA
$DP_{targeted}$	100	100	100	100
$m_{monomer\ added}$ (mg)	400.0	400.0	400.0	400.0
$m_{CTA\ added}$ (mg)	8.0	-	-	-
$m_{TBHP\ added}$ (mg)	0.45	0.30	0.45	0.60
$m_{AsAc\ added}$ (mg)	0.45	0.30	0.45	0.59
$V_{H2O\ added}$ (mL)	0.890	1.272	1.272	1.272
$V_{dioxane\ added}$ (mL)	0.382	-	-	-
% H_2O	70.0	85.0	90.0	92.5
V_{total} (mL)[a]	1.672	3.343	5.015	6.687
$[Mon]_0$ (mol.L^{-1})[b]	2.00	1.00	0.67	0.50
$[TBHP]_0$ (mol.L^{-1})[c]	$3.00\ 10^{-3}$	$1.00\ 10^{-3}$	$1.00\ 10^{-3}$	$1.00\ 10^{-4}$
$[AsAc]_0$ (mol.L^{-1})[c]	$1.50\ 10^{-3}$	$5.00\ 10^{-4}$	$5.00\ 10^{-4}$	$5.00\ 10^{-5}$
$[PABTC]_0/[TBHP]_0$[d]	6.7	10.0	6.7	5.0

[a] Represents the sum of the volume of the monomer added + volume of solvent + V_{total} from the previous block. [b] Represents the concentration of the monomer at the beginning of each block extension. [c] The concentration of TBHP/AsAc at the beginning of each block, assuming full consumption of both TBHP and AsAc in the previous block. [d] The theoretical ratio of PABTC chain transfer agent to TBHP oxidant, assuming full consumption of TBHP in previous block.

Table S12 - Monomer conversion and DMF-SEC analysis of $(PHEA_{100})_4$ prepared *via* RAFT in H_2O/dioxane at 25 °C using TBHP/AsAc redox pair as initiator.

Block	Multiblock poly(2-hydroxyethyl acrylate) composition	Overall monomer conversion (%)[a]	$M_{n,th}$ ($g.mol^{-1}$)[b]	$M_{n,SEC}$ ($g.mol^{-1}$)[c]	$Đ$[c]
1	$PHEA_{100}$	>99	11800	22200	1.11
2	$PHEA_{100}$-*b*-$PHEA_{100}$	>99	23200	50900	1.13
3	$PHEA_{100}$-*b*-$PHEA_{100}$-*b*-$PHEA_{100}$	>99	35100	67300	1.21
4	$PHEA_{100}$-*b*-$PHEA_{100}$-*b*-$PHEA_{100}$-*b*-$PHEA_{100}$	>99	46700	80600	1.50

[a] Determined by ^1H NMR using eq. 1. [b] Determined using eq. 2. [c] Determined using DMF-SEC

Table S13 - Conditions used in preparation of the low DP acrylamido heptablock copolymer *via* RAFT in H_2O/dioxane at 25 °C using TBHP/AsAc redox pair as initiator.

Block	1	2	3	4	5	6	7
Monomer	NAM	NIPAM	NAM	DMA	NAM	DEA	NAM
$DP_{targeted}$	10	10	10	10	10	10	10
$m_{monomer\ added}$ (mg)	600.0	481.0	600.0	421.0	600.0	540.6	600.0
$m_{CTA\ added}$ (mg)	101.3	-	-	-	-	-	-
$m_{TBHP\ added}$ (mg)	0.77	0.77	0.38	0.64	0.59	2.25	0.77
$m_{AsAc\ added}$ (mg)	0.75	0.75	0.37	0.62	0.58	2.20	0.75
$V_{H2O\ added}$ (mL)	0.617	1.417	0.882	0.979	0.882	0.806	0.882
$V_{dioxane\ added}$ (mL)	0.265	-	-	-	-	-	-
% H_2O	70.0	88.5	91.7	93.6	94.7	95.5	96.1
V_{total} (mL)[a]	1.417	2.883	4.250	5.666	7.083	8.500	9.917
$[Mon]_0$ (mol.L^{-1})[b]	3.00	1.50	1.00	0.75	0.60	0.50	0.43
$[TBHP]_0$ (mol.L^{-1})[c]	6.00 10^{-3}	2.93 10^{-3}	9.76 10^{-4}	1.22 10^{-3}	9.02 10^{-4}	2.87 10^{-3}	8.38 10^{-4}
$[AsAc]_0$ (mol.L^{-1})[c]	3.00 10^{-3}	1.47 10^{-3}	4.88 10^{-4}	6.10 10^{-4}	4.51 10^{-4}	1.44 10^{-8}	4.19 10^{-4}
$[PABTC]_0/[TBHP]_0$[d]	50	51	102	61	67	17	51

[a] Represents the sum of the volume of the monomer added + volume of solvent + V_{total} from the previous block. [b] Represents the concentration of the monomer at the beginning of each block extension. [c] The concentration of TBHP/AsAc at the beginning of each block, assuming full consumption of both TBHP and AsAc in the previous block. [d] The theoretical ratio of PABTC chain transfer agent to TBHP oxidant, assuming full consumption of TBHP in previous block.

Table S14 - Monomer conversion and DMF-SEC analysis of the low DP acrylamido heptablock copolymer prepared *via* RAFT in H_2O/dioxane at 25 °C using TBHP/AsAc redox pair as initiator.

Block	Multiblock copolymer composition	Overall monomer conversion (%)[a]	$M_{n,th}$ ($g.mol^{-1}$)[b]	$M_{n,SEC}$ ($g.mol^{-1}$)[c]	$Đ$[c]
1	$PNAM_{10}$	99	1600	1100	1.13
2	$PNAM_{10}$-*b*-$PNIPAM_{10}$	99	2800	2800	1.13
3	$PNAM_{10}$-*b*-$PNIPAM_{10}$-*b*-$PNAM_{10}$	99	4200	4400	1.13
4	$PNAM_{10}$-*b*-$PNIPAM_{10}$-*b*-$PNAM_{10}$-*b*-$PDMA_{10}$	99	5100	6200	1.11
5	$PNAM_{10}$-*b*-$PNIPAM_{10}$-*b*-$PNAM_{10}$-*b*-$PDMA_{10}$-*b*-$PNAM_{10}$	>99	6500	7900	1.09
6	$PNAM_{10}$-*b*-$PNIPAM_{10}$-*b*-$PNAM_{10}$-*b*-$PDMA_{10}$-*b*-$PNAM_{10}$-*b*-$PDEA_{10}$	>99	7800	9400	1.12
7	$PNAM_{10}$-*b*-$PNIPAM_{10}$-*b*-$PNAM_{10}$-*b*-$PDMA_{10}$-*b*-$PNAM_{10}$-*b*-$PDEA_{10}$-*b*-$PNAM_{10}$	>99	9200	11200	1.15

[a] Determined by ^1H NMR using eq. 1. [b] Determined using eq. 2. [c] Determined using DMF-SEC

Table S15 - Conditions used in preparation of the high DP acrylamido pentablock copolymer *via* RAFT in H_2O/dioxane at 25 °C using TBHP/AsAc redox pair as initiator.

Block	1	2	3	4	5
Monomer	NAM	DMA	NIPAM	DEA	NAM
$DP_{targeted}$	100	100	100	100	100
$m_{monomer\ added}$ (mg)	600.0	421.3	481.0	541.0	600.0
$m_{CTA\ added}$ (mg)	10.1	-	-	-	-
$m_{TBHP\ added}$ (mg)	0.13	0.26	0.36	0.64	0.66
$m_{AsAc\ added}$ (mg)	0.06	0.25	0.35	0.62	0.65
$V_{H2O\ added}$ (mL)	0.794	0.979	2.125	0.806	1.590
$V_{dioxane\ added}$ (mL)	0.088	-	-	-	-
% H_2O	90.0	95.3	97.8	98.2	98.6
V_{total} (mL)[a]	1.417	2.833	4.958	6.375	8.500
$[Mon]_0$ (mol.L^{-1})[b]	3.00	1.31	0.69	0.86	0.50
$[TBHP]_0$ (mol.L^{-1})[c]	1.00 10^{-3}	1.00 10^{-3}	8.01 10^{-4}	1.11 10^{-3}	8.62 10^{-4}
$[AsAc]_0$ (mol.L^{-1})[c]	2.50 10^{-4}	5.00 10^{-4}	4.00 10^{-4}	5.55 10^{-4}	4.31 10^{-4}
$[PABTC]_0/[TBHP]_0$[d]	30.0	15.0	11.0	6.0	6.0

[a] Represents the sum of the volume of the monomer added + volume of solvent + V_{total} from the previous block. [b] Represents the concentration of the monomer at the beginning of each block extension. [c] The concentration of TBHP/AsAc at the beginning of each block, assuming full consumption of both TBHP and AsAc in the previous block. [d] The theoretical ratio of PABTC chain transfer agent to TBHP oxidant, assuming full consumption of TBHP in previous block.

Table S16 - Monomer conversion and DMF-SEC analysis of the high DP acrylamido pentablock copolymer prepared *via* RAFT in H_2O/dioxane at 25 °C using TBHP/AsAc redox pair as initiator.

Block	Multiblock copolymer composition	Overall monomer conversion (%)[a]	$M_{n,th}$ ($g.mol^{-1}$)[b]	$M_{n,SEC}$ ($g.mol^{-1}$)[c]	$Đ$[c]
1	$PNAM_{100}$	>99	14400	13100	1.07
2	$PNAM_{100}$-*b*-$PDMA_{100}$	>99	23000	27600	1.10
3	$PNAM_{100}$-*b*-$PDMA_{100}$-*b*-$PNIPAM_{100}$	>99	32100	47300	1.16
4	$PNAM_{100}$-*b*-$PDMA_{100}$-*b*-$PNIPAM_{100}$-*b*-$PDEA_{100}$	>99	48400	62700	1.24
5	$PNAM_{100}$-*b*-$PDMA_{100}$-*b*-$PNIPAM_{100}$-*b*-$PDEA_{100}$-*b*-$PNAM_{100}$	>99	62500	78300	1.30

[a] Determined by ^1H NMR using eq. 1. [b] Determined using eq. 2. [c] Determined using DMF-SEC

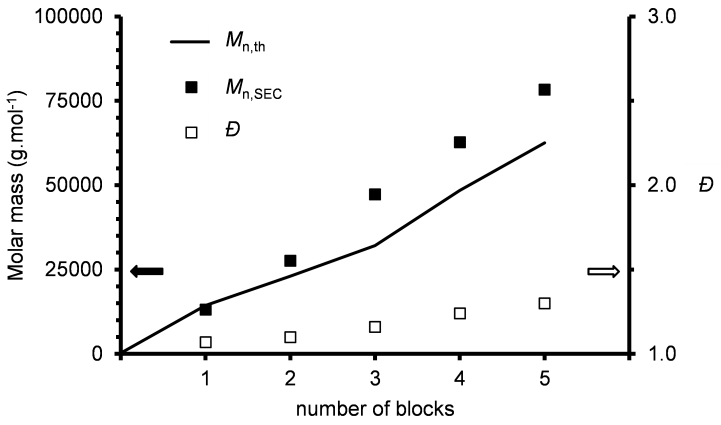


Figure S7 - Evolution of molar mass and dispersity values (determined by DMF-SEC) with each block extension for the high DP acrylamido pentablock copolymer prepared *via* RAFT in H_2O/dioxane at 25 °C using TBHP/AsAc redox pair as initiator.

Table S17 - Conditions used in preparation of the low DP acrylate heptablock copolymer *via* RAFT in H_2O/dioxane at 25 °C using TBHP/AsAc redox pair as initiator.

Block	1	2	3	4	5	6	7
Monomer	HEA	PEGA	CEA	EGMEA	HEA	PEGA	EGMEA
$DP_{targeted}$	10	5	10	10	10	5	10
$m_{monomer\ added}$ (mg)	303.3	626.9	376.5	339.9	303.3	626.9	339.9
$m_{CTA\ added}$ (mg)	62.3	-	-	-	-	-	-
$m_{TBHP\ added}$ (mg)	1.18	0.28	3.24	0.88	0.93	0.68	1.32
$m_{AsAc\ added}$ (mg)	1.16	0.27	3.2	0.87	0.92	0.67	1.31
$V_{H2O\ added}$ (mL)	0.399	0.078	0.561	0.534	0.571	0.296	0.534
$V_{dioxane\ added}$ (mL)	0.171	-	-	-	-	-	-
% H_2O	70.0	73.6	85.8	90.2	92.6	93.4	94.6
V_{total} (mL)[a]	0.871	1.524	2.394	3.265	4.136	5.006	5.877
$[Mon]_0$ (mol.L^{-1})[b]	3.00	0.86	1.09	0.80	0.63	0.26	0.44
$[TBHP]_0$ (mol.L^{-1})[c]	1.50 10^{-2}	2.00 10^{-3}	1.50 10^{-2}	3.00 10^{-3}	2.50 10^{-3}	1.50 10^{-3}	2.50 10^{-3}
$[AsAc]_0$ (mol.L^{-1})[c]	7.50 10^{-3}	1.00 10^{-3}	7.50 10^{-3}	1.50 10^{-3}	1.25 10^{-3}	7.50 10^{-4}	1.25 10^{-3}
$[PABTC]_0/[TBHP]_0$[d]	20.0	85.7	7.3	26.7	25.3	34.8	17.8

[a] Represents the sum of the volume of the monomer added + volume of solvent + V_{total} from the previous block. [b] Represents the concentration of the monomer at the beginning of each block extension. [c] The concentration of TBHP/AsAc at the beginning of each block, assuming full consumption of both TBHP and AsAc in the previous block. [d] The theoretical ratio of PABTC chain transfer agent to TBHP oxidant, assuming full consumption of TBHP in previous block.

Table S18 - Monomer conversion and DMF-SEC analysis of the low DP acrylate heptablock copolymer prepared *via* RAFT in H_2O/dioxane at 25 °C using TBHP/AsAc redox pair as initiator.

Block	Multiblock copolymer composition	Overall monomer conversion (%)[a]	$M_{n,th}$ ($g.mol^{-1}$)[b]	$M_{n,SEC}$ ($g.mol^{-1}$)[c]	$Đ$[c]
1	$PHEA_{10}$	>99	1400	3300	1.19
2	$PHEA_{10}$-*b*-$PPEGA_5$	>99	3800	5800	1.17
3	$PHEA_{10}$-*b*-$PPEGA_5$-*b*-$PCEA_{10}$	>99	5200	7700	1.15
4	$PHEA_{10}$-*b*-$PPEGA_5$-*b*-$PCEA_{10}$-*b*-$PEGMEA_{10}$	>98	6500	10000	1.20
5	$PHEA_{10}$-*b*-$PPEGA_5$-*b*-$PCEA_{10}$-*b*-$PEGMEA_{10}$-*b*-$PHEA_{10}$	>98	7600	13400	1.18
6	$PHEA_{10}$-*b*-$PPEGA_5$-*b*-$PCEA_{10}$-*b*-$PEGMEA_{10}$-*b*-$PHEA_{10}$-*b*-$PPEGA_5$	>98	10000	16700	1.23
7	$PHEA_{10}$-*b*-$PPEGA_5$-*b*-$PCEA_{10}$-*b*-$PEGMEA_{10}$-*b*-$PHEA_{10}$-*b*-$PPEGA_5$-*b*-$PEGMEA_{10}$	>98	11200	18400	1.28

[a] Determined by ^1H NMR using eq. 1. [b] Determined using eq. 2. [c] Determined using DMF-SEC

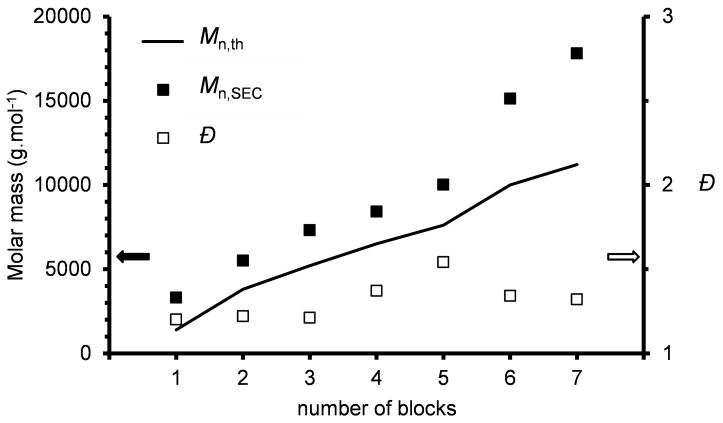


Figure S8 - Evolution of molar mass and dispersity values (determined by DMF-SEC) with each block extension for the low DP acrylate heptablock copolymer prepared *via* RAFT in H_2O/dioxane at 25 °C using TBHP/AsAc redox pair as initiator.

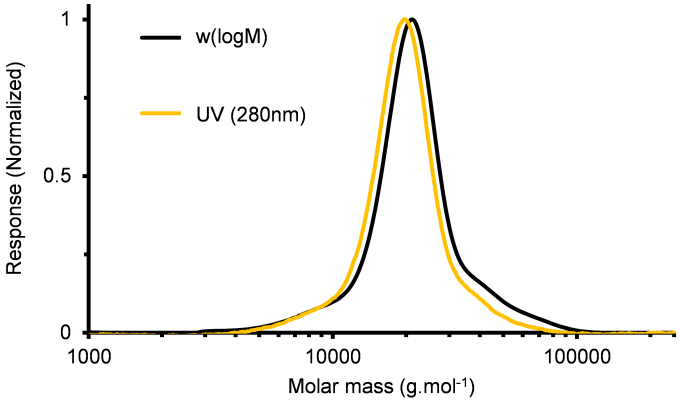


Figure S9 - DMF-SEC chromatogram of the low DP acrylate heptablock copolymer prepared *via* RAFT in H_2O/dioxane at 25 °C using TBHP/AsAc redox pair as initiator, showing the (normalized) w(log M) and 280 nm UV detector responses.

Table S19 - Conditions used in preparation of the low DP acrylate octablock copolymer (blocks 1-4, 5b-8b) and the low DP acrylate/acrylamido heptablock copolymer (1-4, 5a-7a) *via* RAFT in H_2O/dioxane at 25 °C using TBHP/AsAc redox pair as initiator. The polymerization mixture was split into two after the first 4 blocks and each half was block extended to prepare the two different multiblock copolymers.

Block	1	2	3	4	5a	6a	7a	5b	6b	7b	8b
Monomer	HEA	AA	PEGA	MA	NAM	NIPAM	DMA	HEA	EGMEA	PEGA	HEA
$DP_{targeted}$	10	10	5	10	10	10	10	10	10	5	10
$m_{monomer\ added}$ (mg)	303.3	188.2	626.9	224.9	184.4	147.8	129.5	151.7	170.0	313.4	151.7
$m_{CTA\ added}$ (mg)	62.3	-	-	-	-	-	-	-	-	-	-
$m_{TBHP\ added}$ (mg)	1.18	2.91	0.42	0.97	0.45	0.76	0.77	0.45	0.54	0.39	0.61
$m_{AsAc\ added}$ (mg)	1.16	2.88	0.42	0.96	0.44	0.75	0.76	0.44	0.54	0.38	0.60
$V_{H2O\ added}$ (mL)	0.399	0.567	0.150	0.511	0.271	0.435	0.301	0.285	0.267	0.148	0.372
$V_{dioxane\ added}$ (mL)	0.171	-	-	-	-	-	-	-	-	-	-
% H_2O	70.0	85.0	86.7	90.5	92.7	94.7	95.5	92.8	94.1	94.7	95.7
V_{total} (mL)[a]	0.871	1.138	1.863	2.610	1.740	2.175	2.611	1.74	2.175	2.323	2.696
$[Mon]_0$ ($mol.L^{-1}$)[b]	3.00	1.62	0.56	0.85	0.66	0.54	0.46	0.66	0.54	0.23	0.39
$[TBHP]_0$ ($mol.L^{-1}$)[c]	$1.50\ 10^{-2}$	$2.00\ 10^{-2}$	$2.00\ 10^{-3}$	$3.50\ 10^{-3}$	$2.50\ 10^{-3}$	$3.50\ 10^{-3}$	$3.00\ 10^{-3}$	$2.50\ 10^{-3}$	$2.50\ 10^{-3}$	$1.50\ 10^{-3}$	$2.00\ 10^{-3}$
$[AsAc]_0$ ($mol.L^{-1}$)[c]	$7.50\ 10^{-3}$	$1.00\ 10^{-2}$	$1.00\ 10^{-3}$	$1.75\ 10^{-3}$	$1.25\ 10^{-3}$	$1.75\ 10^{-3}$	$1.50\ 10^{-3}$	$1.25\ 10^{-3}$	$1.25\ 10^{-3}$	$7.5\ 10^{-4}$	$1.00\ 10^{-3}$
$[PABTC]_0/[TBHP]_0$[d]	20.0	8.1	55.8	24.2	26.4	15.5	15.3	26.4	21.6	30.5	19.4

[a] Represents the sum of the volume of the monomer added + volume of solvent + V_{total} from the previous block. [b] Represents the concentration of the monomer at the beginning of each block extension. [c] The concentration of TBHP/AsAc at the beginning of each block, assuming full consumption of both TBHP and AsAc in the previous block. [d] The theoretical ratio of PABTC chain transfer agent to TBHP oxidant, assuming full consumption of TBHP in previous block.

Table S20 - Monomer conversion and DMF-SEC analysis of the low DP acrylate octablock copolymer (blocks 1-4, 5b-8b) and the low DP acrylate/acrylamido heptablock copolymer (1-4, 5a-7a) prepared *via* RAFT in H_2O/dioxane at 25 °C using TBHP/AsAc redox pair as initiator.

Block	Multiblock copolymer composition	Overall monomer conversion (%)[a]	$M_{n,th}$ ($g.mol^{-1}$)[b]	$M_{n,SEC}$ ($g.mol^{-1}$)[c]	$Đ$[c]
1	$PHEA_{10}$	>99	1400	3200	1.19
2	$PHEA_{10}$-b-PAA_{10}	96	2100	3100	1.23
3	$PHEA_{10}$-*b*-PAA_{10}-*b*-$PPEGA_5$	>99	4500	7000	1.22
4	$PHEA_{10}$-*b*-PAA_{10}-*b*-$PPEGA_5$-*b*-PMA_{10}	>99	5300	8400	1.27
5a	$PHEA_{10}$-*b*-PAA_{10}-*b*-$PPEGA_5$-*b*-PMA_{10}-*b*-$PNAM_{10}$	>99	6700	9000	1.33
6a	$PHEA_{10}$-*b*-PAA_{10}-*b*-$PPEGA_5$-*b*-PMA_{10}-*b*-$PNAM_{10}$-*b*-$PNIPAM_{10}$	>99	7900	13000	1.20
7a	$PHEA_{10}$-*b*-PAA_{10}-*b*-$PPEGA_5$-*b*-PMA_{10}-*b*-$PNAM_{10}$-*b*-$PNIPAM_{10}$-*b*-$PDMA_{10}$	>99	8800	15500	1.24
5b	$PHEA_{10}$-*b*-PAA_{10}-*b*-$PPEGA_5$-*b*-PMA_{10}-*b*-$PHEA_{10}$	>99	6500	11600	1.26
6b	$PHEA_{10}$-*b*-PAA_{10}-*b*-$PPEGA_5$-*b*-PMA_{10}-*b*-$PHEA_{10}$-*b*-$PEGMEA_{10}$	>99	7800	12500	1.38
7b	$PHEA_{10}$-*b*-PAA_{10}-*b*-$PPEGA_5$-*b*-PMA_{10}-*b*-$PHEA_{10}$-*b*-$PEGMEA_{10}$-*b*-$PPEGA_5$	>99	10200	16700	1.42
8b	$PHEA_{10}$-*b*-PAA_{10}-*b*-$PPEGA_5$-*b*-PMA_{10}-*b*-$PHEA_{10}$-*b*-$PEGMEA_{10}$-*b*-$PPEGA_5$-*b*-$PHEA_{10}$	>99	11300	20800	1.34

[a] Determined by ^1H NMR using eq. 1. [b] Determined using eq. 2.[c] Determined using DMF-SEC

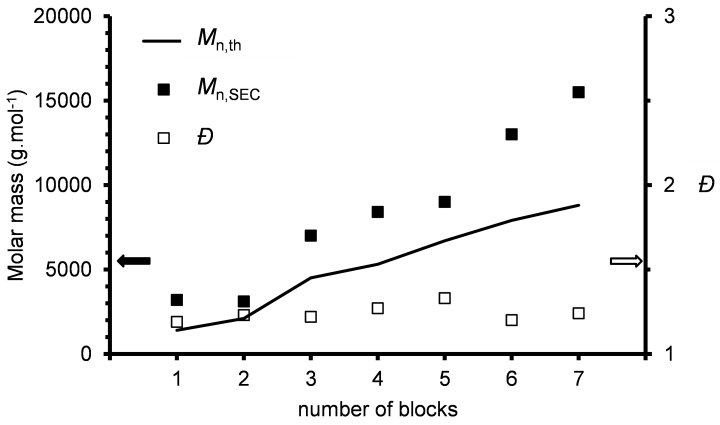


Figure S10 - Evolution of molar mass and dispersity values (determined by DMF-SEC) with each block extension for the low DP acrylate/acrylamido heptablock copolymer prepared *via* RAFT in H_2O/dioxane at 25 °C using TBHP/AsAc redox pair as initiator.

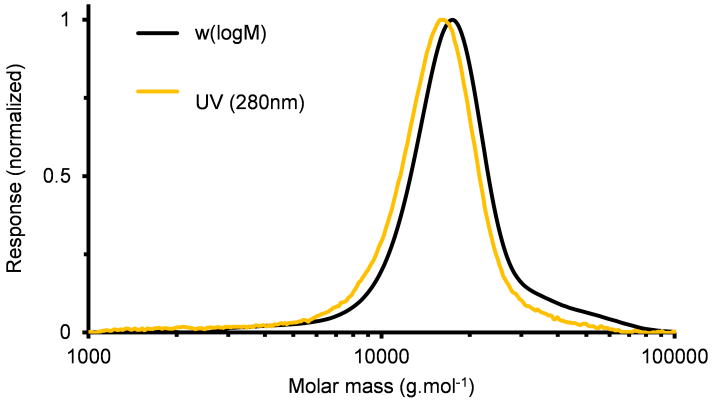


Figure S11 - DMF-SEC chromatogram of the low DP acrylate/acrylamido heptablock copolymer prepared *via* RAFT in H_2O/dioxane at 25 °C using TBHP/AsAc redox pair as initiator, showing the (normalized) w(log M) and 280 nm UV detector responses.

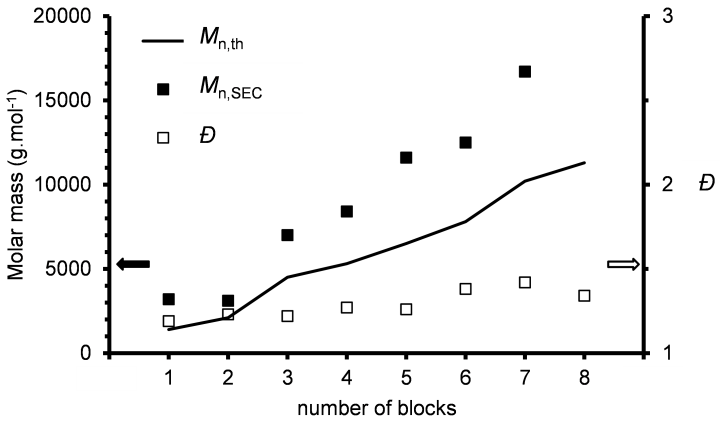


Figure S12 - Evolution of molar mass and dispersity values (determined by DMF-SEC) with each block extension for the low DP acrylate octablock copolymer prepared *via* RAFT in H_2O/dioxane at 25 °C using TBHP/AsAc redox pair as initiator.

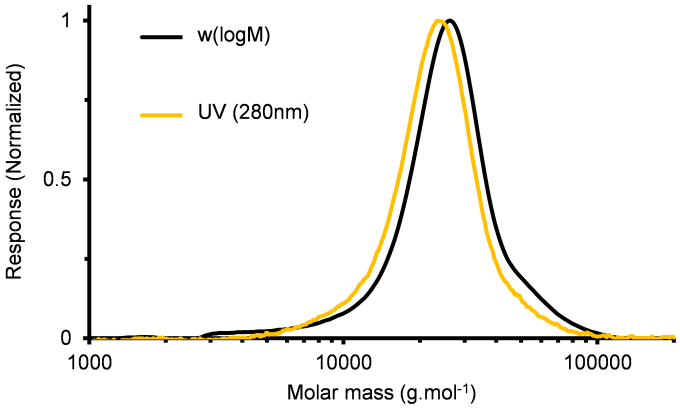


Figure S13 - DMF-SEC chromatogram of the low DP acrylate octablock copolymer prepared *via* RAFT in H_2O/dioxane at 25 °C using TBHP/AsAc redox pair as initiator, showing the (normalized) w(log M) and 280 nm UV detector responses.

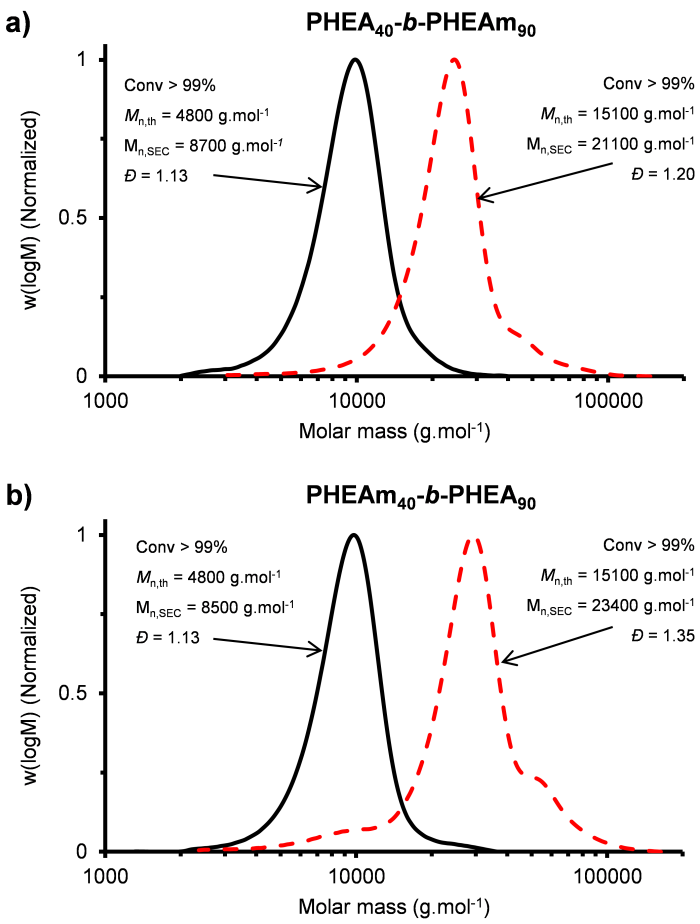


Figure S14 - DMF-SEC chromatograms for diblock copolymers a) $PHEA_{40}$-*b*-$PHEAm_{90}$ and b) $PHEAm_{40}$-*b*-$PHEA_{90}$) prepared in one-pot *via* RAFT in H_2O/dioxane at 44 °C using VA-044 as thermal azoinitiator. Note the high molecular weight shoulders are due to diacrylate impurity in the HEA non-purified monomer (Figure S3)

Table S21- Summary of conditions and characterization of $PHEA_{40}$-*b*-$PHEAm_{90}$ and $PHEAm_{40}$-*b*-$PHEA_{90}$ diblocks prepared in one-pot *via* RAFT in H_2O/dioxane at 44 °C using VA-044 as initiator.

Diblock copolymer composition	$[M]_0$ ($mol.L^{-1}$)[a]	$[PABTC]_0$ ($mol.L^{-1}$)	$[VA\text{-}044]_0$ ($mol.L^{-1}$)[b]	$[PABTC]_0$/$[VA\text{-}044]_0$	Monomer Conversion (%)[c]	$M_{n,th}$ ($g.mol^{-1}$)[d]	$M_{n,SEC}$ ($g.mol^{-1}$)[e]	$Đ$[e]
$PHEA_{40}$	4.0	0.10	10.0	10	>99	4800	8700	1.13
$PHEA_{40}$-*b*-$PHEAm_{90}$	2.8	0.03	19.7	22	>99	15100	21200	1.20
$PHEAm_{40}$	4.0	0.10	10.0	10	>99	4800	8500	1.13
$PHEAm_{40}$-*b*-$PHEA_{90}$	2.8	0.03	19.7	22	>99	15100	23400	1.35

[a] Represents the concentration of the monomer at the beginning of each block extension. [b] Takes into account the amount of initiator added and the amount od initiator remaining following the synthesis of the previous block. [c] Determined by ^1H NMR using eq. 1. [d] Determined using eq. 2. [e] Determined using DMF-SEC.