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Electronic Supplementary Information

Synthesis of Ultra-High Molecular Weight ABA Triblock Copolymers via Aqueous RAFT-mediated Gel Polymerisation, End Group Modifications and Chain Coupling

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Materials

Acrylic acid (AA, Aldrich, 99%) was pre-treated with basic aluminium oxide (Acros Organics) to remove the radical inhibitor monomethyl ether hydroquinone (MEHQ) prior to use. Acrylamide (AM, Sigma, 99%), 3-(((1-carboxyethyl)thio)-carbonothioyl)thio)propanoic acid (CETCTP, Boron Molecular, 90%), ammonium persulfate (APS, Sigma-Aldrich, 98%), sodium formaldehyde sulfoxylate dihydrate (SFS, Aldrich, 98%), *n*-butylamine (Sigma-Aldrich, 99.5%), sodium nitrate (Merck, 99.9%), sodium bicarbonate (Merck, 99.9%), *N,N*-dimethylformamide (DMF, Ajax FineChem, 99.9%), water (deionised and Milli-Q grades), deuterium oxide (Merck, 99.9%) were used as received without further purification.

Synthesis of Polymers A1 to A8 by RAFT Polymerisation of AA

The homopolymers of AA (polymers **A1** to **A8**) were synthesised according to the general procedure outlined in the main manuscript. The quantities of monomer, RAFT reagent, internal standard, solvent, and initiators employed for the synthesis of these polymers are detailed in Table 1.

Table S1. Quantities of reagents and solvent used in the synthesis of polymers A1 to A8.

	Polymer Entry							
	A1	**A2**	**A3**	**A4**	**A5**	**A6**	**A7**	**A8**
AA	5.78 mL[a] 46.3 mmol							
CETCTP	84.8 mg 0.333 mmol	42.4 mg 0.167 mmol	28.3 mg 0.111 mmol	21.2 mg 0.083 mmol	17.0 mg 0.067 mmol	8.50 mg 0.033 mmol	2.83 mL[b] 0.022 mmol	2.12 mL[b] 0.017 mmol
DMF	0.30 mL[c]							
H_2O	2.10 mL	3.16 mL	3.52 mL	3.69 mL	3.80 mL	4.01 mL	1.26 mL	2.00 mL
APS	1.27 mL[d] 0.056 mmol	634 µL[d] 0.028 mmol	423 µL[d] 0.019 mmol	317 µL[d] 0.014 mmol	254 µL[d] 0.011 mmol	127 µL[d] 0.006 mmol	85 µL[d] 0.004 mmol	63 µL[d] 0.003 mmol
SFS	856 µL[e] 0.056 mmol	428 µL[e] 0.028 mmol	285 µL[e] 0.019 mmol	214 µL[e] 0.014 mmol	171 µL[e] 0.011 mmol	86 µL[e] 0.006 mmol	57 µL[e] 0.004 mmol	43 µL[e] 0.003 mmol

[a] An 57.6 wt% (8 M) stock solution of AA was prepared and utilised for the synthesis of all polymers A1 to A8. [b] A 0.2 wt% stock solution of RAFT agent CETCTP was prepared and utilised for the synthesis of polymers A7 and A8. [c] DMF was used as an internal standard for monitoring of monomer conversion. [d] A 1.0 wt% stock solution of APS was prepared and utilised for the synthesis of all polymers A1 to A8. [e] A 1.0 wt% stock solution of SFS was prepared and utilised for the synthesis of all polymers A1 to A8.

Synthesis of Polymers AB1 to AB8 by RAFT Polymerisation of AM

The AB diblock copolymers of AA and AM (polymers **AB1** to **AB8**) were also synthesised according to the general procedure outlined in the main manuscript. Note that the synthesis of each AB diblock copolymer employed the same numbered A block as the macro chain transfer agent (macro-CTA). For example, polymer **A1** was used as the macro-CTA for the synthesis of polymer **AB1**. The quantities of monomer, RAFT reagent, internal standard, solvent, and initiators employed for the synthesis of these polymers are detailed in Table 2.

Table S2. Quantities of reagents and solvent used in the synthesis of polymers AB1 to AB8

	Polymer Entry							
	AB1	**AB2**	**AB3**	**AB4**	**AB5**	**AB6**	**AB7**	**AB8**
AA	5.86 mL[a] 46.9 mmol							
CTA	8.7 mg 1.67 µmol	13.1 mg 1.11 µmol	23.2 mg 1.11 µmol	28.2 mg 0.83 µmol	38.1 mg 0.83 µmol	56.5 mg 0.67 µmol	78.7 mg 0.67 µmol	115 mg 0.67 µmol
DMF	0.30 mL[b]							
H_2O	4.13 mL	4.13 mL	4.13 mL	4.13 mL	4.13 mL	4.13 mL	4.13 mL	4.13 mL
APS	7 µL[c] 0.28 µmol	4 µL[c] 0.19 µmol	4 µL[c] 0.19 µmol	3 µL[c] 0.14 µmol	3 µL[c] 0.14 µmol	3 µL[c] 0.14 µmol	3 µL[c] 0.14 µmol	3 µL[c] 0.14 µmol
SFS	5 µL[d] 0.28 µmol	3 µL[d] 0.19 µmol	3 µL[d] 0.19 µmol	2 µL[d] 0.14 µmol	2 µL[d] 0.14 µmol	2 µL[d] 0.14 µmol	2 µL[d] 0.14 µmol	2 µL[d] 0.14 µmol

[a] An 56.9 wt% (8 M) stock solution of AM was prepared and utilised for the synthesis of all polymers AB1 to AB8. [b] DMF was used as an internal standard for monitoring of monomer conversion. [c] A 1.0 wt% stock solution of APS was prepared and utilised for the synthesis of all polymers AB1 to AB8. [d] A 1.0 wt% stock solution of SFS was prepared and utilised for the synthesis of all polymers AB1 to AB8.

Controlled Synthesis of an ABA Triblock Copolymer by RAFT Polymerisation

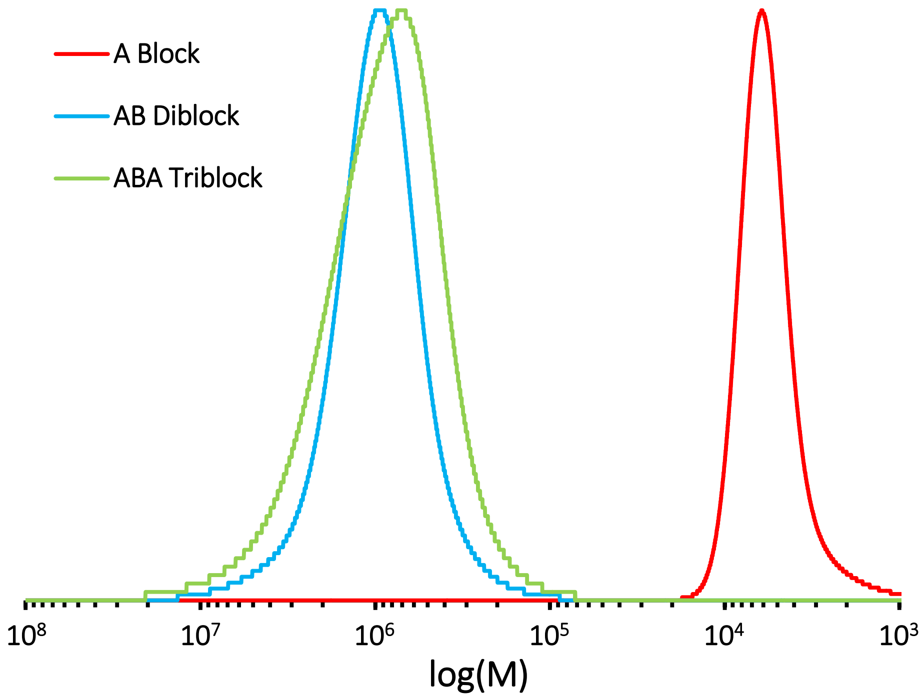
A controlled experiment was performed to synthesise an ABA triblock copolymer using only RAFT polymerisation. A similar derivative of AB diblock copolymer **AB1** (M_n = 626 k, $Đ$ = 1.46) was used as the macro-CTA for the second chain extension stage with AA to see whether the chain would grow efficiently. The quantities of monomer, macro-CTA, solvent, and initiators employed for this reaction is detailed in Table 3.

Table S3. Quantities of reagents and solvent used in the second chain extension stage using RAFT polymerisation.

AA	Macro-CTA	DMF	H_2O	APS	SFS
5.78 mL[a] 46.3 mmol	0.928 g 1.48 µmol	0.30 mL[b]	4.19 mL	6 µL[c] 0.25 µmol	4 µL[d] 0.25 µmol

[a] An 57.6 wt% (8 M) stock solution of AA was prepared and utilised for this chain extension step. [b] DMF was used as an internal standard for monitoring of monomer conversion. [c] A 1.0 wt% stock solution of APS was prepared and utilised for this reaction. [d] A 1.0 wt% stock solution of SFS was prepared and utilised for this reaction.

The polymerisation was conducted for 24 hours and the final monomer conversion was determined to be approximately 4%. The final molecular weight (M_n) of the polymer was analysed with SEC and determined to be 566 k ($Đ$ = 1.80). An overlay of the SEC traces for the A block, the AB diblock copolymer and the ABA triblock copolymer from this polymerisation is shown in Figure 1 below.



FigureS 1. Overlay of SEC chromatograms for the A block, AB diblock and ABA triblock copolymers from the second chain extension step using only RAFT polymerisation.

Aminolysis of AB Diblock Copolymers AB1 to AB8

AB diblock copolymers **AB1** to **AB8** were subjected to aminolysis using *n*-butylamine as the nucleophilic reagent according to the general procedure outlined in the main manuscript. The final optimised quantities of *n*-butylamine used for the aminolysis reactions are shown in Table 4.

Table S4. Quantities of *n*-butylamine in the synthesis of polymers ABA1 to ABA8

	Polymer Entry							
	ABA1	**ABA2**	**ABA3**	**ABA4**	**ABA5**	**ABA6**	**ABA7**	**ABA8**
Polymer Concentration	50 mg of the AB Diblock Copolymer in 10 mL of H_2O (0.5 wt%)							
[$BuNH_2$]: [C=S] Ratio	20,000:1	20,000:1	20,000:1	131,000:1	176,000:1	654,000:1	911,000:1	1,330,000:1
[$BuNH_2$]: [COOH] Ratio	278:1	122:1	69:1	278:1	278:1	556:1	556:1	556:1
V(*n*-$BuNH_2$) (mL)	0.177	0.182	0.197	1.20	1.70	5.40	7.00	11.3
Reaction Time (h)	6	8	12	6	24	2	4	24

Screening Polymerisations for the Synthesis of the AB Diblock Copolymers

Each of the macro-CTA (polymers **A1** to **A8**) were initially subjected to polymerisation at 20°C for 24 hours, with three initial monomer to macro-CTA ratios (DP_{target})ranging from 28,100 to 56,300. The ratios between the macro-CTA and the redox initiators were initially maintained at 6:1:1. The monomer conversion (obtained by ^{1}H NMR) and the SEC data for these screening polymerisations are shown in Table 5 and Table 6.

Table S5. Monomer conversions obtained from the initial screening polymerisations of the AB diblock copolymers.

Macro-CTA	$M_{n,SEC}$ of Macro CTA (×10³)	DP_{target}		
		28,100	42,200	56,300
A1	5.21	77%	73%	63%
A2	11.8	61%	67%	41%
A3	20.9	65%	70%	46%
A4	33.9	68%	57%	55%
A5	45.7	49%	54%	51%
A6	84.8	52%	51%	47%
A7	118	18%	18%	22%
A8	173	16%	20%	15%

Monomer conversion was determined by ^{1}H NMR at the 24 hours mark with DMF as the internal standard.

TableS 6. SEC data obtained from the initial screening polymerisations of the AB diblock copolymers.

Macro-CTA	$M_{n,SEC}$ of Macro-CTA (×10³)	DP_{target}					
		28,100		42,200		56,300	
		$M_{n,SEC}$ (×10³)	$Đ$	$M_{n,SEC}$ (×10³)	$Đ$	$M_{n,SEC}$ (×10³)	$Đ$
A1	5.21	557	1.49	705	1.65	610	1.63
A2	11.8	403	1.31	542	1.44	517	1.24
A3	20.9	355	1.33	502	1.39	490	1.20
A4	33.9	336	1.36	456	1.22	537	1.32
A5	45.7	311	1.22	352	1.31	513	1.21
A6	84.8	291	1.24	359	1.30	440	1.36
A7	118	221	1.19	279	1.21	370	1.27
A8	173	252	1.20	304	1.22	306	1.21

Molecular weight and dispersity data were determined using aqueous SEC calibrated with PAA standards.

Screening Reactions for the Aminolysis of AB Diblock Copolymer AB1

Six different aminolysis reactions were initially performed on AB diblock copolymer AB1. Two polymer concentrations (0.5 and 1.0 wt%) were used. Three different molar excess ratios of *n*-butylamine to the thiocarbonylthio groups ranging from 2,000 to 200,000 were employed. The changes in molecular weight and dispersity of polymer AB1 were monitored by SEC and these results are shown in Figure 2 to Figure 4.

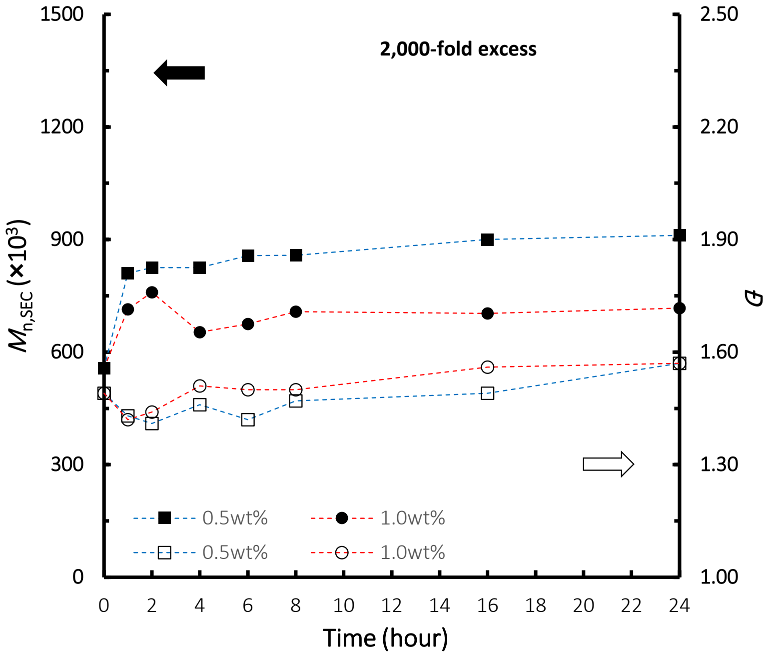


Figure S2. **SEC data for the aminolysis of polymer AB1 at 0.5 and 1.0 wt% using an *n*-butylamine excess of 2,000-fold.**

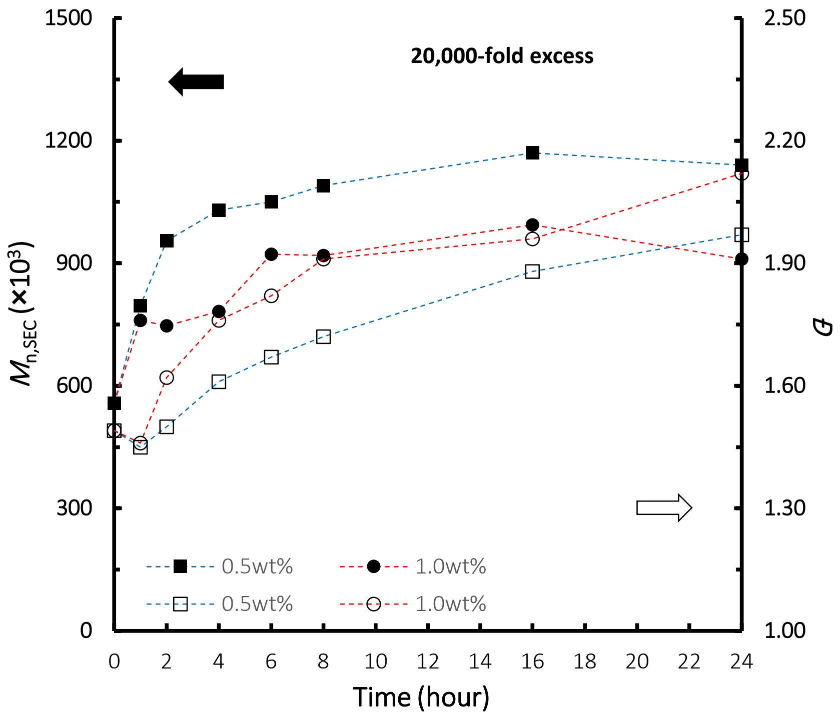


Figure S3. **SEC data for the aminolysis of polymer AB1 at 0.5 and 1.0 wt% using an *n*-butylamine excess of 20,000-fold.**

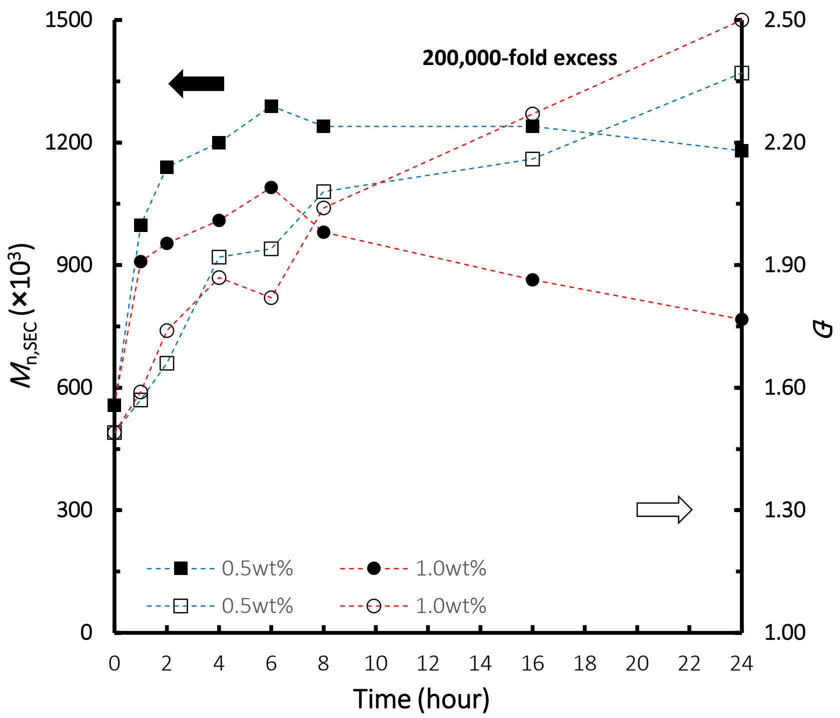


Figure S4. SEC data for the aminolysis of polymer AB1 at 0.5 and 1.0 wt% using an *n*-butylamine excess of 200,000-fold.

Screening Reactions for the Aminolysis of AB Diblock Copolymers AB2 to AB8

AB diblock copolymers **AB2** to **AB8** were subjected to aminolysis reactions with an initial concentration of 0.5 wt%. The ratio of *n*-butylamine to thiocarbonylthio functionality was maintained at 20,000. SEC was used to monitor the molecular weight growth over 24 hours. The changes in molecular weight and dispersity for polymers **AB2** to **AB8** is detailed in Table 7.

Table S7. SEC data for the aminolysis of polymer AB2 to AB8 using an *n*-butylamine excess of 20,000-fold.

Reaction Time (hour)	$M_{n,SEC}$ (×10³) / *Đ*						
	AB2	**AB3**	**AB4**	**AB5**	**AB6**	**AB7**	**AB8**
0	542 1.44	502 1.39	537 1.32	513 1.21	602 1.51	641 1.36	582 1.23
6	937 1.65	943 1.59	880 1.45	733 1.30	938 1.99	853 1.74	662 1.50
8	1,000 1.68	960 1.61	879 1.53	749 1.33	889 2.15	813 1.79	666 1.56
10	1,070 1.69	979 1.61	925 1.52	768 1.34	1,110 1.88	741 2.08	708 1.51
12	1,050 1.76	1,000 1.67	945 1.53	815 1.36	989 2.12	776 2.00	703 1.59
14	1,090 1.77	936 1.76	970 1.55	801 1.37	1,090 2.14	835 1.98	651 1.64
16	1,090 1.82	1,020 1.74	990 1.59	810 1.41	874 2.45	841 1.98	668 1.64
24	1,160 1.78	1,030 1.70	991 1.60	801 1.40	961 2.50	852 2.14	704 1.70

Molecular weight and dispersity data were determined using aqueous SEC calibrated with PAA standards.

Screening Reactions for the Aminolysis of AB Diblock Copolymers AB1 to AB8 at pH 8

AB diblock copolymers **AB1** to **AB8** were subjected to aminolysis reactions with an initial concentration of 0.5wt%. The initial pH of these reaction mixtures ranged from approximately 4.0 to 4.5 depending on the chain length of the A blocks. The pH of these reaction mixtures was adjusted to approximately 8 using sodium hydroxide solution. The ratio of *n*-butylamine to thiocarbonylthio functionality was once again maintained at 20,000 for comparison between low pH and high pH. SEC was used to monitor the molecular weight growth over 24 hours. The changes in molecular weight and dispersity for polymers **AB1** to **AB8** is detailed in Table 8.

Table S8. SEC data for the aminolysis of polymer AB1 to AB8 at pH 8 using an *n*-butylamine excess of 20,000-fold.

Reaction Time (hour)	$M_{n,SEC}$ (×10³) / *Đ*							
	AB1	**AB2**	**AB3**	**AB4**	**AB5**	**AB6**	**AB7**	**AB8**
0	557 1.49	542 1.44	502 1.39	537 1.32	513 1.21	602 1.51	641 1.36	582 1.23
6	883 1.78	912 1.63	829 1.59	816 1.49	722 1.31	949 2.03	823 1.83	672 1.54
8	952 1.81	933 1.72	898 1.67	881 1.58	732 1.36	927 2.12	847 1.83	732 1.52
10	965 1.98	857 1.94	843 1.53	952 1.53	779 1.33	853 2.43	782 1.99	630 1.61
12	919 2.04	965 1.90	879 1.72	819 1.69	740 1.40	849 2.43	776 2.01	675 1.57
14	924 2.16	943 1.92	758 1.95	789 1.72	789 1.40	812 2.20	772 1.99	612 1.66
16	937 2.23	898 1.99	968 1.82	887 1.72	739 1.44	997 2.30	774 2.31	636 1.72
24	797 2.38	852 2.16	795 2.04	782 1.84	759 1.46	763 2.67	694 2.27	632 1.76

Molecular weight and dispersity data were determined using aqueous SEC calibrated with PAA standards.

Aminolysis Reactions with a [BuNH2]:[COOH] ratios of 278:1 and 556:1

AB diblock copolymers **AB2** to **AB8** were once again subjected to aminolysis reactions with an initial concentration of 0.5 wt%. This time, the ratio of *n*-butylamine to carboxylic functionality on the A blocks was maintained at approximately 278:1 for all polymers. SEC was used to monitor the molecular weight growth over 24 hours. The changes in molecular weight and dispersity for polymers **AB2** to **AB8** is detailed in Table 9.

Table S9. SEC data for the aminolysis of polymer AB2 to AB8 at 0.5 wt% using an [$BuNH_2$]:[COOH] ratio of 278:1.

Reaction Time (hour)	$M_{n,SEC}$ (×10³) / $Đ$						
	AB2	**AB3**	**AB4**	**AB5**	**AB6**	**AB7**	**AB8**
0	542 1.44	502 1.39	537 1.32	513 1.21	602 1.51	641 1.36	582 1.23
6	999 1.71	1,050 1.73	1,050 1.59	862 1.36	1,370 1.95	1,020 2.05	955 1.50
24	1,170 1.99	966 2.18	1,110 1.85	967 1.53	1,060 3.09	1,030 2.36	867 1.93

Molecular weight and dispersity data were determined using aqueous SEC calibrated with PAA standards.

Lastly, AB diblock copolymers AB6 to AB8 were subjected to another set of aminolysis reactions at 0.5 wt% and a [$BuNH_2$]:[COOH] ratio of 556:1. SEC was used to monitor the molecular weight growth over 24 hours. The changes in molecular weight and dispersity for polymers AB6 to AB8 is detailed in Table 10.

Table S10. SEC data for the aminolysis of polymer AB6 to AB8 at 0.5 wt% using an [$BuNH_2$]:[COOH] ratio of 556:1.

Reaction Time (hour)	$M_{n,SEC}$ (×10³) / $Đ$		
	AB6	**AB7**	**AB8**
0	602 1.51	641 1.36	582 1.23
2	1,170 1.59	866 1.60	745 1.24
4	1,360 1.70	1,210 1.49	836 1.27
6	1,440 1.83	1,340 1.54	872 1.29
24	1,600 2.15	1,250 1.80	1,000 1.46

Molecular weight and dispersity data were determined using aqueous SEC calibrated with PAA standards.

SEC Chromatograms of A Block Polymers, AB Diblock and ABA Triblock Copolymers

The overlays of SEC traces for the A blocks (A2 to A8), their corresponding AB diblock copolymers (AB2 to AB8) and ABA triblock copolymers (ABA2 to ABA8) are shown in Figure 5 to Figure 11.

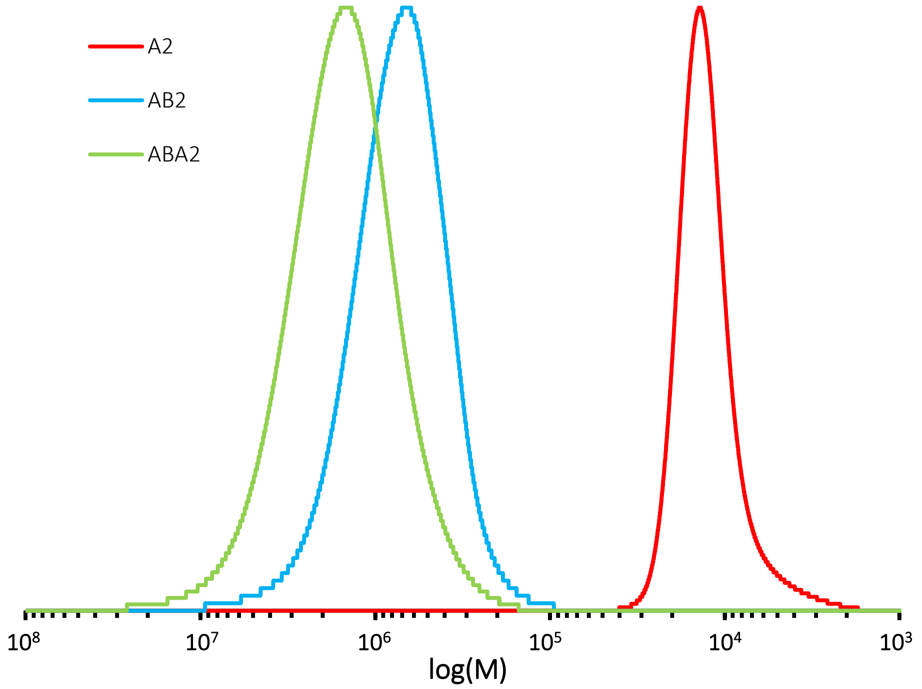


Figure S5. Overlay of SEC chromatograms for polymers A2, AB2 and ABA2.

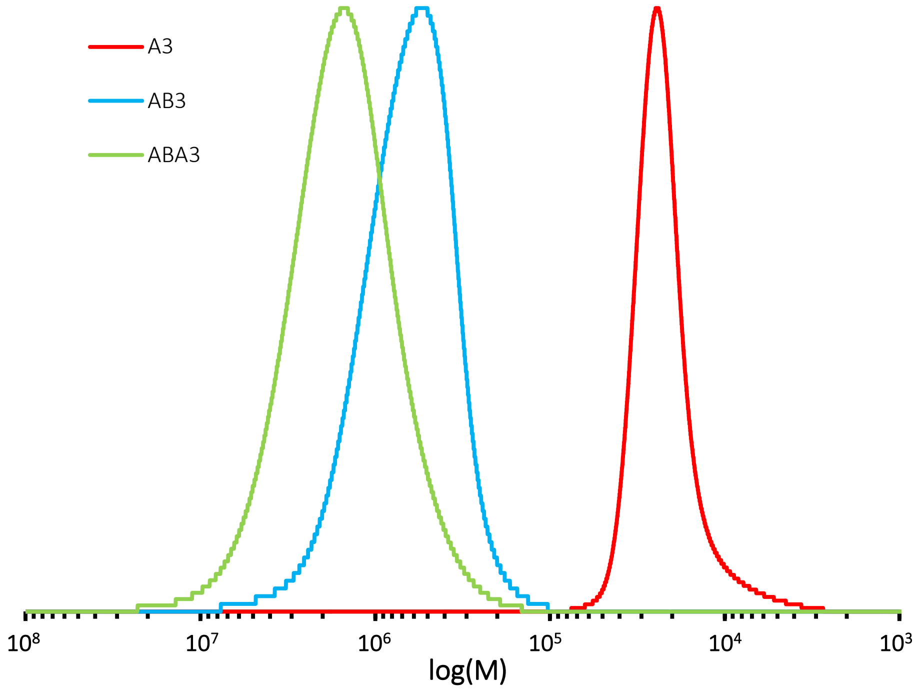


Figure S6. Overlay of SEC chromatograms for polymers A3, AB3 and ABA3.

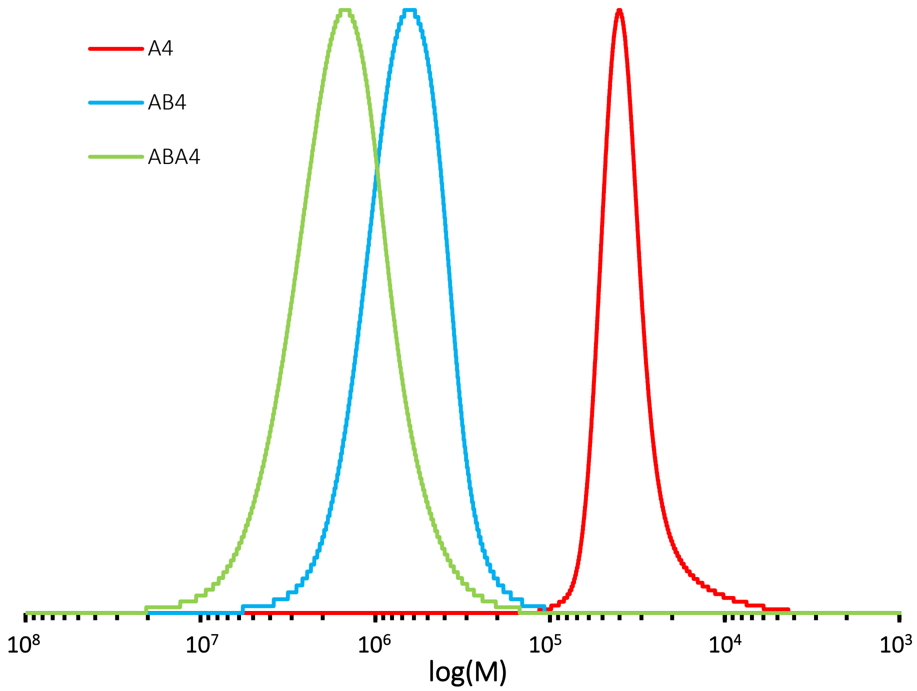


Figure S7. Overlay of SEC chromatograms for polymers A4, AB4 and ABA4.

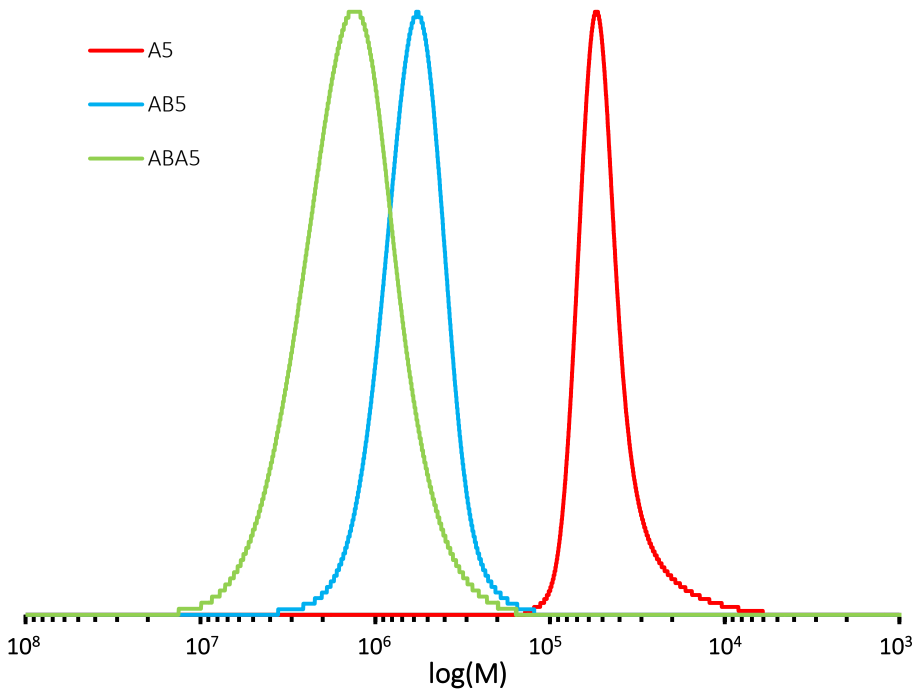


Figure S8. Overlay of SEC chromatograms for polymers A5, AB5 and ABA5.

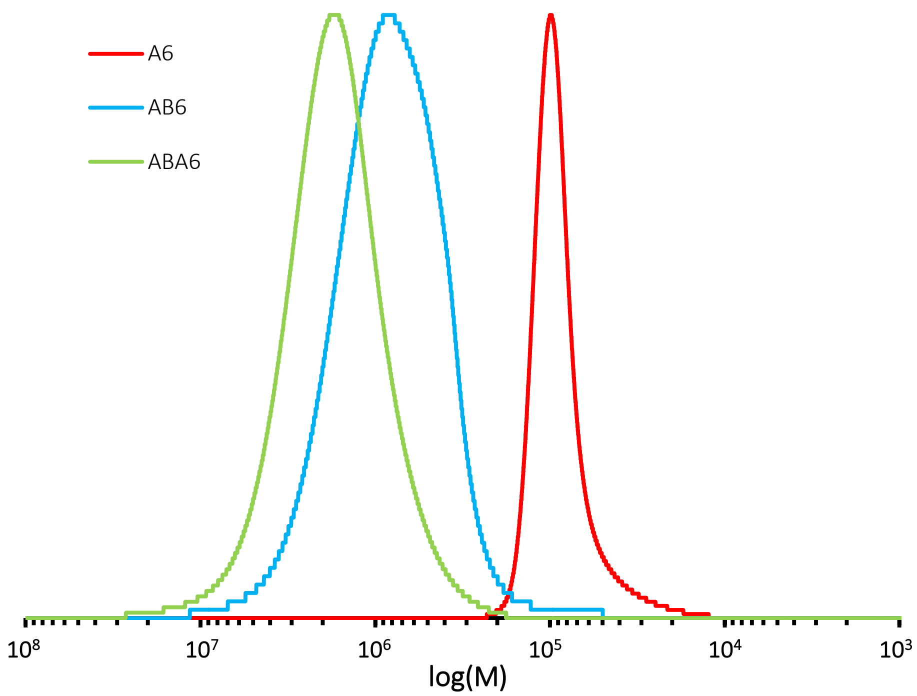


Figure S9. Overlay of SEC chromatograms for polymers A6, AB6 and ABA6.

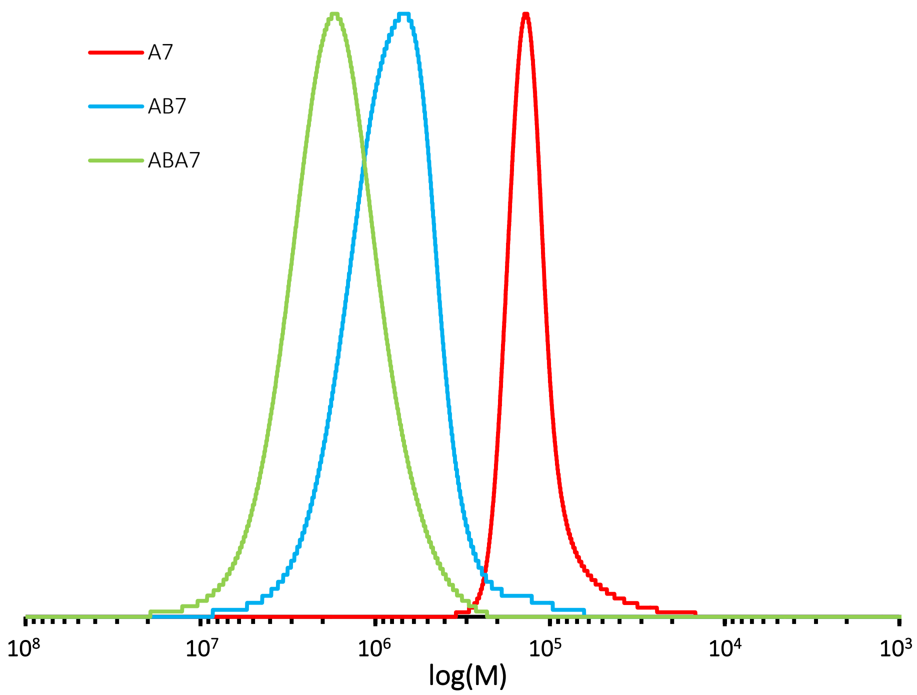


Figure S10. Overlay of SEC chromatograms for polymers A7, AB7 and ABA7.

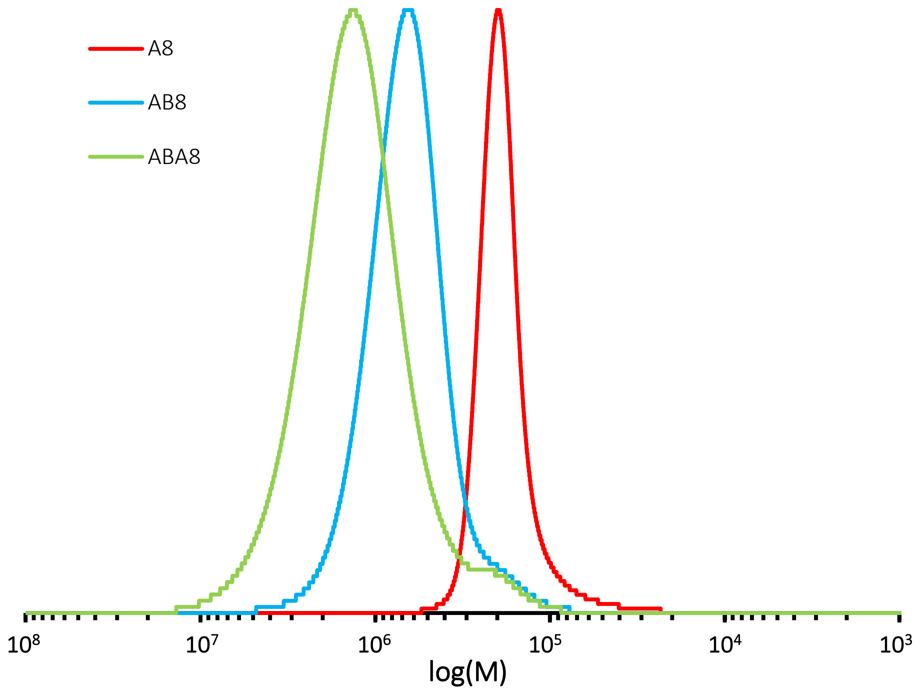


Figure S11. Overlay of SEC chromatograms for polymers A8, AB8 and ABA8.