Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

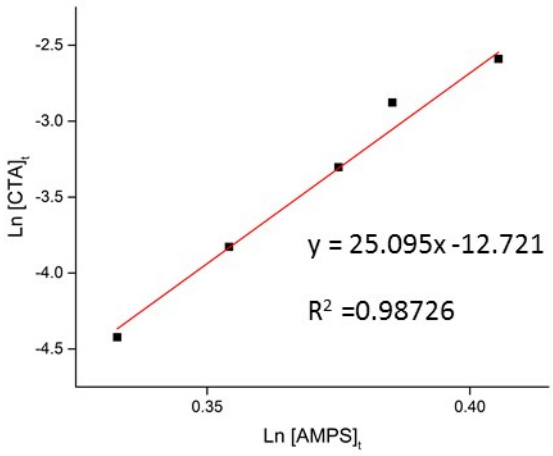

Figure SI1: Walling plot for the polymerization of AMPS monomer targeting a DP of 20 with the chain transfer agent BDMAT (in water at 90 °C)

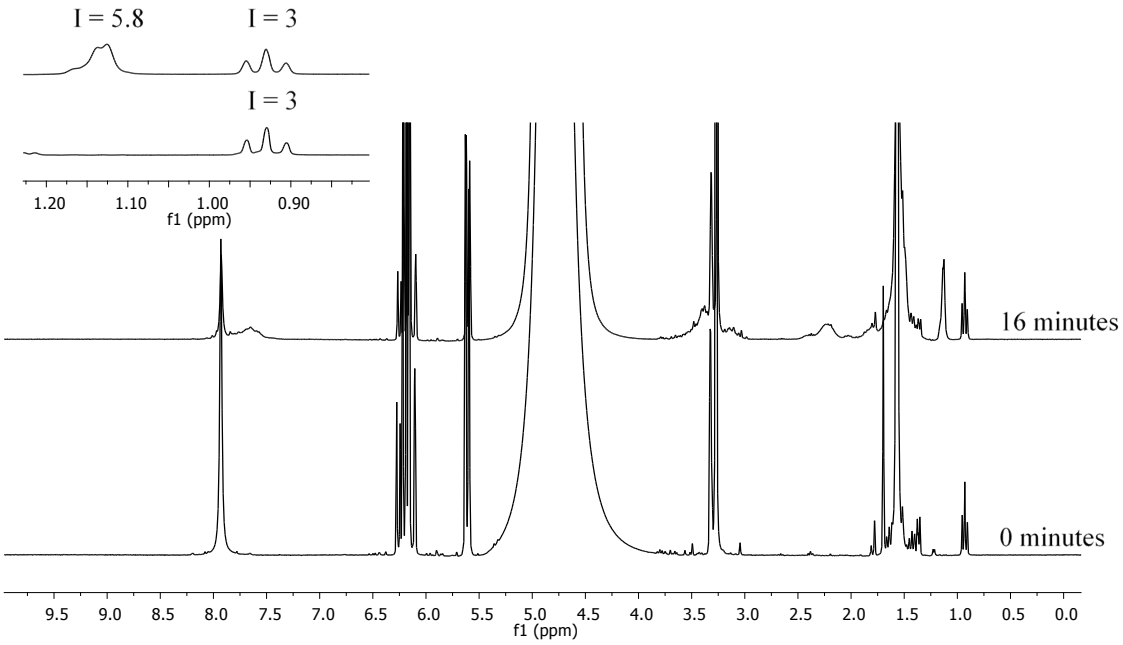

Figure SI2: ^{1}H NMR spectra (D_2O, 300 MHz) showing the chain transfer agent and monomer consumption after 16 minutes of the polymerization of AMPS with BDMAT at 90 °C in water.

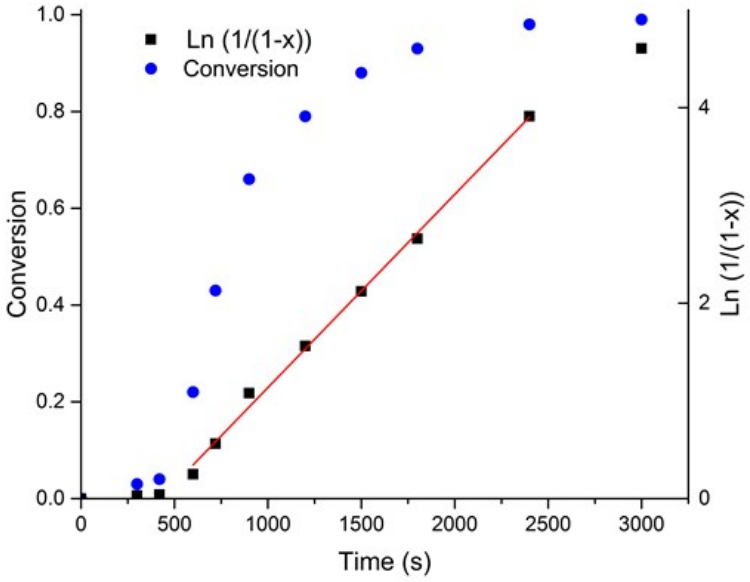

Figure SI3: Conversion (Blue) and pseudo-first order plot (Black) versus the time for the synthesis of the random copolymer $P(AMPS)_{40}$-*co*-$P(HEAm)_{40}$ synthesized in water at 90 °C with VA-086.

Table SI1: Conditions used for the preparation of $(P(AMPS_{10}))_8$ via RAFT polymerization in phosphate buffer solution at 90 °C.

Block	1	2	3	4	5	6	7	8
Monomer	AMPS	AMPS	AMPS	AMPS	AMPS	AMPS	AMPS	AMPS
$DP_{targeted}$	10	10	10	10	10	10	10	10
$m_{monomer\ added}$ (mg)	580	580	580	580	580	580	580	580
m_{CTA} (mg)	64	-	-	-	-	-	-	-
$m_{VA\text{-}086\ added}$ (mg)	1.22	0.85	0.82	0.89	0.96	1.03	1.11	1.17
m_{NaOH} (mg)	5.06	-	-	-	-	-	-	-
m_{H2O} (mg)	358	-	-	-	-	-	-	-
V_{total} (mL)[a]	1.7	2.5	3.4	4.3	5.2	6.0	6.9	7.8
$VA\text{-}086_{consumed}$ (%)[b]	20	11	11	11	11	11	11	11
$m_{VA\text{-}086\ total}$ (mg)[c]	1.22	1.83	2.46	3.08	3.72	4.35	4.99	5.62
$[AMPS]_0$ (M)[d]	1.50	1.00	0.74	0.59	0.49	0.42	0.37	0.32
$[CTA]_t/[VA\text{-}086]_0$	60	40	30	24	20	17	15	13
$[CTA]_t/[VA\text{-}086]_{consumed}$	301	380	282	225	186	159	139	123
L (%)[e]	99.7	99.8	99.8	99.8	99.8	99.8	99.8	99.8
Cumulative L (%)[f]	99.7	99.5	99.3	99.1	99.0	98.8	98.6	98.5

[a] Represents the sum of the volume of the monomer added + V_{total} from the previous block. [b] Determined using the following equation $VA\text{-}086_{consumed} = [VA\text{-}086]_{consumed}/[VA\text{-}086]_0 *100 = 2f(1\text{-}exp(\text{-}k_d t))(1\text{-}f_c/2)*100$ with f = 0.5, f_c = 0, k_d = $3.1x10^{-5}$ s^{-1}. [c] Represents the total weight of VA-086 at the start of each chain extension characterised by the sum of the weight of VA-086 added plus the weight of VA-086 remaining from the previous block. [d] Represents the concentration of the monomer at the beginning of each block extension. [e] Theoretical estimation of the fraction of living chains per block. [f] Theoretical estimation of the cumulated fraction of living chains

Table SI2: ^{1}H NMR and SEC data analysis for the multiblock homopolymer $(P(AMPS)_{10})_8$ after chain extension

Block	Multiblock composition	Monomer conversion[a] (%)	$M_{n,th}$[b] (g mol^{-1})	$M_{n,SEC}$[c] (g mol^{-1})	$Đ$[c]
1	$P(AMPS)_{10}$	99	2,500	5,700	1.09
2	$P(AMPS)_{10}$-*b*-$P(AMPS)_{10}$	99	4,800	8,300	1.09
3	$P(AMPS)_{10}$-*b*-$P(AMPS)_{10}$-*b*-$P(AMPS)_{10}$=	> 99	7,100	9,600	1.09
4	$P(AMPS)_{10}$-*b*-$P(AMPS)_{10}$-*b*-$P(AMPS)_{10}$-*b*-$P(AMPS)_{10}$	> 99	9,300	12,300	1.10
5	$P(AMPS)_{10}$-*b*-$P(AMPS)_{10}$-*b*-$P(AMPS)_{10}$-*b*-$P(AMPS)_{10}$-*b*-$P(AMPS)_{10}$	> 99	11,600	14,800	1.12
6	$P(AMPS)_{10}$-*b*-$P(AMPS)_{10}$-*b*-$P(AMPS)_{10}$-*b*-$P(AMPS)_{10}$-*b*-$P(AMPS)_{10}$-*b*-$P(AMPS)_{10}$	> 99	13,900	17,000	1.13
7	$P(AMPS)_{10}$-*b*-$P(AMPS)_{10}$-*b*-$P(AMPS)_{10}$-*b*-$P(AMPS)_{10}$-*b*-$P(AMPS)_{10}$-*b*-$P(AMPS)_{10}$-*b*-$P(AMPS)_{10}$	> 99	16,200	17,700	1.16
8	$P(AMPS)_{10}$-*b*-$P(AMPS)_{10}$-*b*-$P(AMPS)_{10}$-*b*-$P(AMPS)_{10}$-*b*-$P(AMPS)_{10}$-*b*-$P(AMPS)_{10}$-*b*-$P(AMPS)_{10}$-*b*-$P(AMPS)_{10}$	> 99	18,400	18,900	1.18

[a] Determined by ^{1}H NMR in MeOD. [b] Determined using equation 2. [c] Determined using aqueous SEC with a RI detector using PEG as a standard.

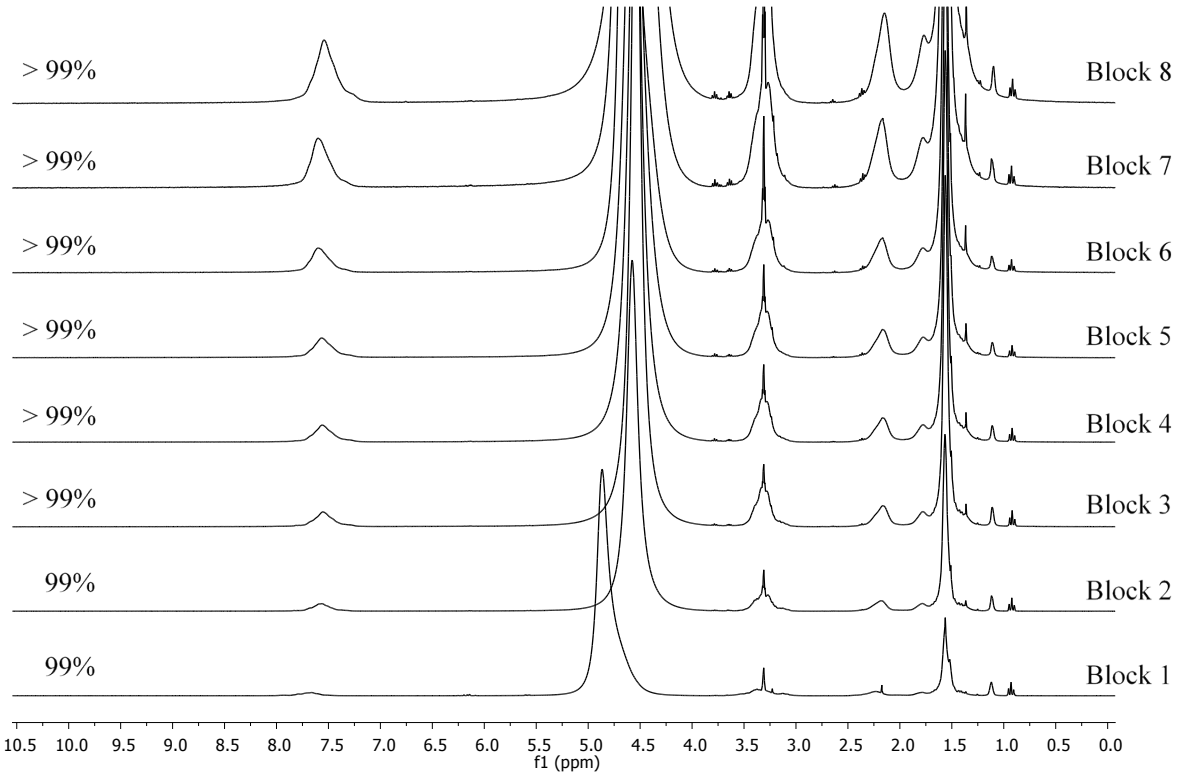

Figure SI4: ^{1}H NMR spectra (MeOD, 300 MHz) displaying the monomer conversion for each new chain extension (up to 8 blocks).

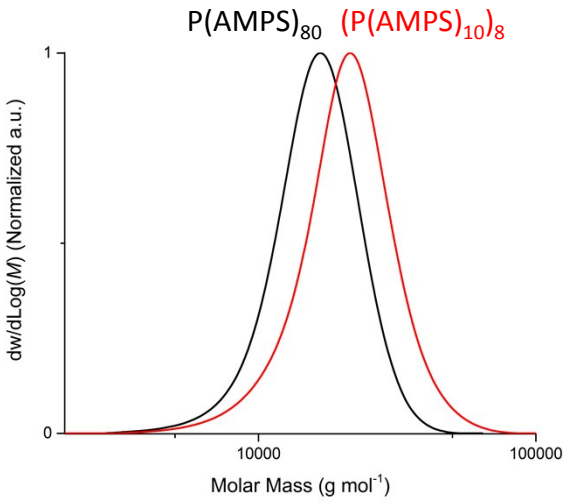

Figure SI5: Comparison of the final SEC chromatograms (aqueous SEC using PEG standard) obtained for the homopolymer $P(AMPS)_{80}$ and the 8th blocks of the octablock $(P(AMPS)_{10})_8$ synthesized by RAFT polymerization.

Table SI3: Conditions used for the preparation of $(P(AMPS)_{10}$-*b*-$P(HEAm)_{10})_4$ via RAFT polymerization in phosphate buffer solution at 90 °C.

Block	1	2	3	4	5	6	7	8
Monomer	AMPS	HEAm	AMPS	HEAm	AMPS	HEAm	AMPS	HEAm
$DP_{targeted}$	10	10	10	10	10	10	10	10
$m_{monomer\ added}$ (mg)	580	292	580	292	580	292	580	292
m_{CTA} (mg)	64	-	-	-	-	-	-	-
$m_{VA\text{-}086\ added}$ (mg)	1.22	0.47	0.91	0.43	1.08	0.53	1.25	0.64
$M_{NaOH\ added}$ (mg)	5.06	-	-	-	-	-	-	-
V_{H2O}	358	-	-	-	-	-	-	-
V_{total} (mL)[a]	1.69	1.99	2.85	3.15	4.01	4.33	5.19	5.51
$VA\text{-}086_{consumed}$ (%)[b]	1.22	1.42	2.06	2.26	2.89	3.11	3.73	3.98
$m_{VA\text{-}086\ total}$ (mg)[c]	20	20	11	20	11	20	11	20
$[AMPS]_0$ (M)[d]	1.50	1.27	0.89	0.80	0.63	0.59	0.49	0.46
$[CTA]_t/[VA\text{-}086]_0$	60	51	36	32	25	23	20	18
$[CTA]_t/[VA\text{-}086]_{consumed}$	301	255	338	161	240	117	186	92
L (%)[e]	99.7	99.7	99.8	99.7	99.8	99.7	99.8	99.7
Cumulative L (%)[f]	99.7	99.3	99.2	98.8	98.7	98.3	98.2	97.8

[a] Represents the sum of the volume of the monomer added + V_{total} from the previous block. [b] Determined using the following equation $VA\text{-}086_{consumed} = [VA\text{-}086]_{consumed}/[VA\text{-}086]_0 *100 = 2f(1\text{-}\exp(\text{-}k_d t))(1\text{-}f_c/2)*100$ with $f = 0.5$, $f_c = 0$, $k_d = 3.1\text{x}10^{-5}\ s^{-1}$. [c] Represents the total weight of VA-086 at the start of each chain extension characterised by the sum of the weight of VA-086 added plus the weight of VA-086 remaining from the previous block. [d] Represents the concentration of the monomer at the beginning of each block extension. [e] Theoretical estimation of the fraction of living chains per block. [f] Theoretical estimation of the cumulated fraction of living chains

Table SI4: ^{1}H NMR and SEC data analysis for the multiblock copolymer $(P(AMPS)_{10}$-*b*-$P(HEAm)_{10})_4$ after chain extension

Block	Multiblock composition	Monomer conversion[a] (%)	$M_{n,th}$[b] (g mol^{-1})	$M_{n,SEC}$[c] (g mol^{-1})	$Đ$[c]
1	$P(AMPS)_{10}$	99	2,600	5,500	1.09
2	$P(AMPS)_{10}$-*b*-$P(HEAm)_{10}$	99	3,700	4,000	1.25
3	$P(AMPS)_{10}$-*b*-$P(HEAm)_{10}$-*b*-$P(AMPS)_{10}$	> 99	6,000	9,100	1.13
4	$P(AMPS)_{10}$-*b*-$P(HEAm)_{10}$-*b*-$P(AMPS)_{10}$-*b*-$P(HEAm)_{10}$	> 99	7,100	8,400	1.18
5	$P(AMPS)_{10}$-*b*-$P(HEAm)_{10}$-*b*-$P(AMPS)_{10}$-*b*-$P(HEAm)_{10}$-*b*-$P(AMPS)_{10}$	> 99	9,400	13,100	1.18
6	$P(AMPS)_{10}$-*b*-$P(HEAm)_{10}$-*b*-$P(AMPS)_{10}$-*b*-$P(HEAm)_{10}$-*b*-$P(AMPS)_{10}$-*b*-$P(HEAm)_{10}$	> 99	10,500	11,800	1.25
7	$P(AMPS)_{10}$-*b*-$P(HEAm)_{10}$-*b*-$P(AMPS)_{10}$-*b*-$P(HEAm)_{10}$-*b*-$P(AMPS)_{10}$-*b*-$P(HEAm)_{10}$-*b*-$P(AMPS)_{10}$	> 99	12,800	17,700	1.30
8	$P(AMPS)_{10}$-*b*-$P(HEAm)_{10}$-*b*-$P(AMPS)_{10}$-*b*-$P(HEAm)_{10}$-*b*-$P(AMPS)_{10}$-*b*-$P(HEAm)_{10}$-*b*-$P(AMPS)_{10}$-*b*-$P(HEAm)_{10}$	> 99	13,900	16,700	1.48

[a] Determined by ^{1}H NMR in MeOD. [b] Determined using equation 2. [c] Determined using aqueous SEC with a RI detector using PEG as a standard.

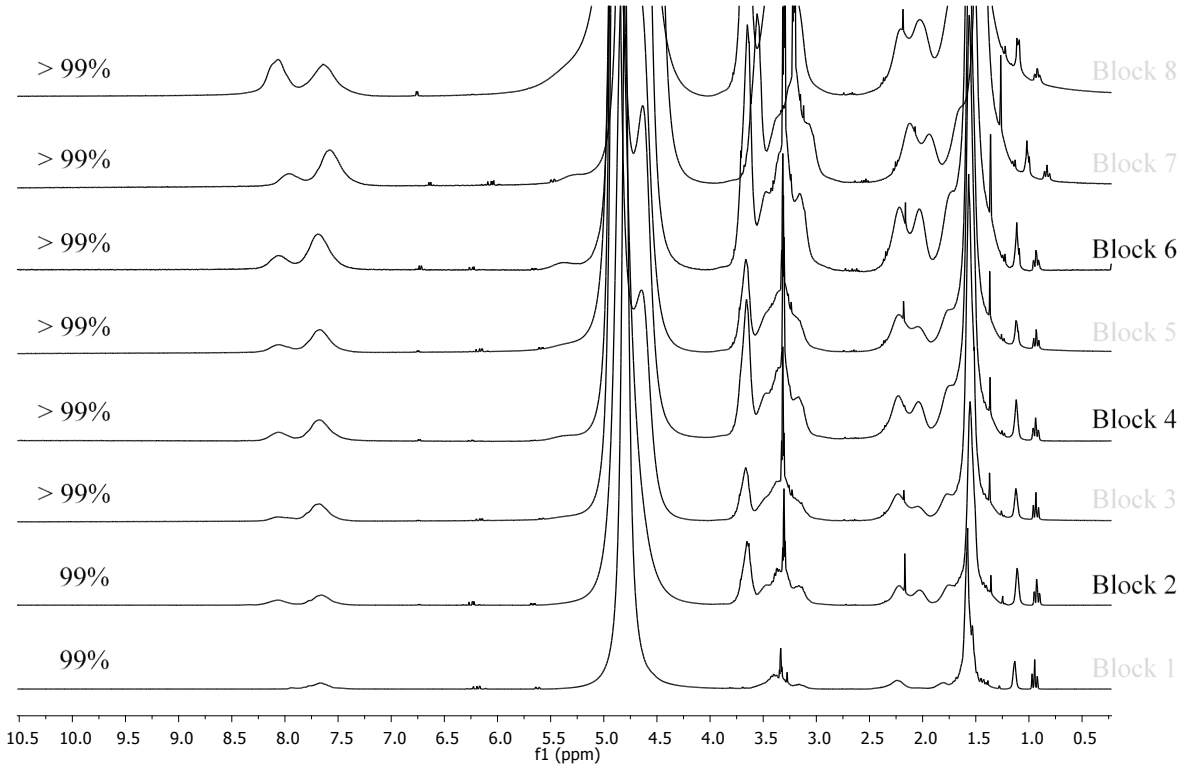

Figure SI6: ^{1}H NMR spectra (MeOD, 300 MHz) displaying the monomer conversion for each new chain extension (up to 8 blocks).

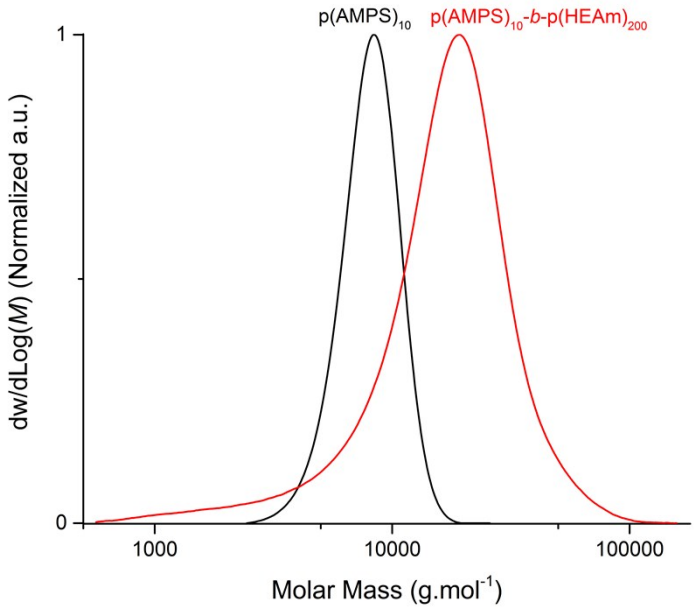

Figure SI7: SEC chromatogram (aqueous SEC with PEG standard) of the macro CTA-PAMPS10 (Black) then chain extended with $PHEAm_{200}$.

Table SI5: Conditions used for the preparation of $(P(AMPS)_{10}$-*b*-$P(NAM)_{10})_2$ via RAFT polymerization in phosphate buffer solution at 90 °C.

Block	1	2	3	4
Monomer	AMPS	NAM	AMPS	NAM
$DP_{targeted}$	10	10	10	10
$m_{monomer\ added}$ (mg)	1160	715	1160	715
m_{CTA} (mg)	128	-	-	-
$m_{VA\text{-}086\ added}$ (mg)	2.43	0.74	1.61	0.97
$M_{NaOH\ added}$ (mg)	10.13	-	-	-
V_{H2O}	1080	-	-	-
V_{total} (mL)[a]	3.38	4.07	5.79	5.63
$VA\text{-}086_{consumed}$ (%)[b]	1.22	1.45	1.98	2.25
$m_{VA\text{-}086\ total}$ (mg)[c]	20	20	11	20
$[AMPS]_0$ (M)[d]	1.50	1.24	0.88	0.90
$[CTA]_t/[VA\text{-}086]_0$	60	50	35	31
$[CTA]_t/[VA\text{-}086]_{consumed}$	301	325	334	203
L (%)[e]	99.6	99.6	99.8	99.7
Cumulative L (%)[f]	99.6	99.3	99.1	98.8

[a] Represents the sum of the volume of the monomer added + V_{total} from the previous block. [b] Determined using the following equation $VA\text{-}086_{consumed} = [VA\text{-}086]_{consumed}/[VA\text{-}086]_0 *100 = 2f(1-\exp(-k_d t))(1-f_c/2)*100$ with $f = 0.5$, $f_c = 0$, $k_d = 3.1\text{x}10^{-5}\ s^{-1}$. [c] Represents the total weight of VA-086 at the start of each chain extension characterised by the sum of the weight of VA-086 added plus the weight of VA-086 remaining from the previous block. [d] Represents the concentration of the monomer at the beginning of each block extension. [e] Theoretical estimation of the fraction of living chains per block. [f] Theoretical estimation of the cumulated fraction of living chains.

Table SI6: ^{1}H NMR and SEC data analysis for the multiblock copolymer (P(AMPS)$_{10}$- *b*-P(NAM)$_{10}$)$_2$ after chain extension

Block	Multiblock composition	Monomer conversion[a] (%)	$M_{n,th}$[b] (g mol^{-1})	$M_{n,SEC}$[c] (g mol^{-1})	$Đ$[c]
1	P(AMPS)$_{10}$	99	2,500	5,400	1.09
2	P(AMPS)$_{10}$-*b*-P(NAM)$_{10}$	99	4,000	1,800	1.50
3	P(AMPS)$_{10}$-*b*-P(NAM)$_{10}$-*b*-P(AMPS)$_{10}$	> 99	6,200	9,100	1.10
4	P(AMPS)$_{10}$-*b*-P(NAM)$_{10}$-*b*-P(AMPS)$_{10}$-*b*-P(NAM)$_{10}$	> 99	7,600	4,000	1.41

[a] Determined by ^{1}H NMR in MeOD. [b] Determined using equation 2. [c] Determined using aqueous SEC with a RI detector using PEG as a standard.

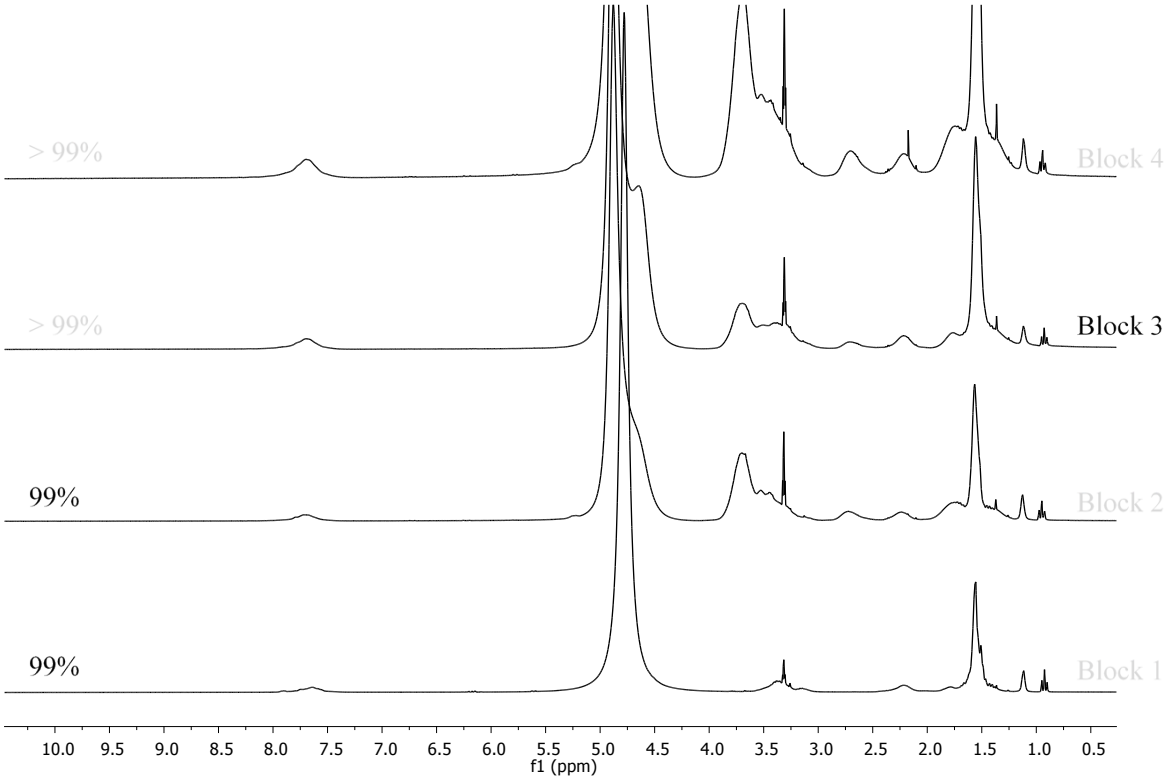

Figure SI8: ^{1}H NMR spectra (MeOD, 300 MHz) displaying the monomer conversion for each new chain extension (up to 4 blocks).

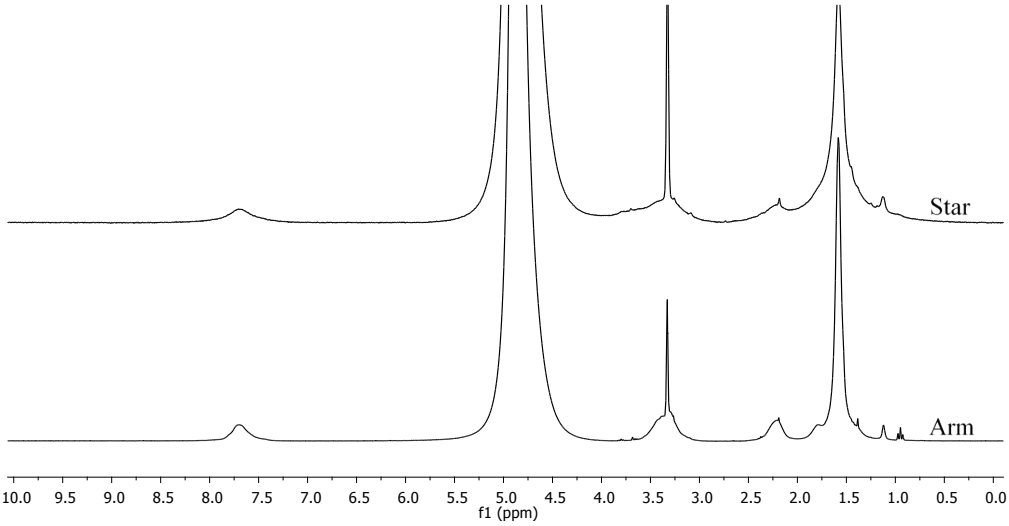

Figure SI9: ^{1}H NMR spectra (MeOD, 300 MHz) showing the monomer conversion for the arm (bottom) after 2 hours and the cross-linker conversion for the star (top) after 2.5 hours.