Electronic Supplementary Information for

Ultrafast RAFT Polymerization: Multiblock Copolymers within Minutes

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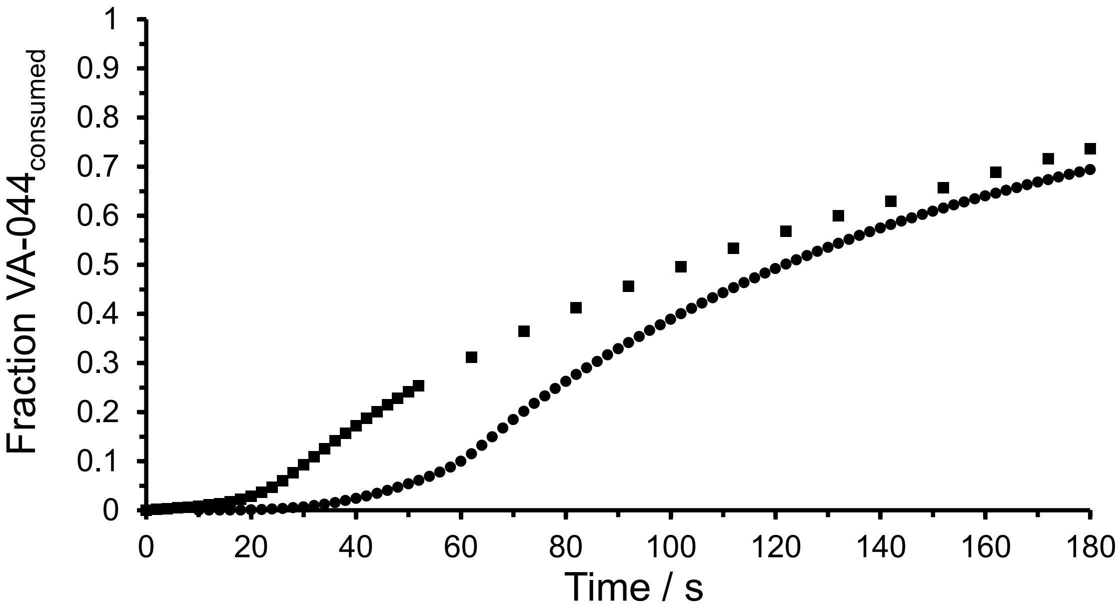

Figure S1. Comparison of the fraction of azoinitiator VA-044 consumed during the 1st block (circles) and the 2nd block (squares) (see Table S2, cycles 1 and 2 for experimental RAFT conditions) calculated using equation S1 (see below) and the temperature profile (Figure S2) obtained during the synthesis of $PNAM_{20}$-*b*-$PNAM_{20}$ via RAFT polymerization in the presence of air and without degassing (oil bath thermostated at 100˚C).

Method to determine the decomposition rate constant k_d

Arrhenius equation: $k_d = A e^{\frac{-E_A}{RT}}$, where k_d is the decomposition rate constant (in s^{-1}) of the azoinitiator, A the pre-exponential factor, E_A the activation energy (in $J.mol^{-1}$), R the Universal gas constant (= 8.31 $J.mol^{-1}.K^{-1}$) and T the temperature (in K).

k_d values for VA-044 are determined by using Equation S1 based on the temperature profile recorded (Figure S5):

$$A = \frac{k_{d(317K)}}{e^{\frac{-E_A}{RT_{(317K)}}}} = \frac{k_{d(x\,K)}}{e^{\frac{-E_A}{RT_{(x\,K)}}}} \qquad \text{(Equation S1)}$$

Where x is the unknown temperature. A value of 108 000 $J.mol^{-1}$ is used for E_A (obtained from Wako, http://www.wako-chem.co.jp/specialty/waterazo/VA-044.htm).

As an example, the table below shows k_d values determined for VA-044 by using Equation S1 and the temperature profile recorded during the first block $PNAM_{20}$.

T (K)	kd(VA-044)	Time (s)	[VA-044]t	[VA-044]consumed
301.800	2.44E-06	6	1.000	0.000
301.500	2.34E-06	8	1.000	0.000
312.200	1.02E-05	10	1.000	0.000
318.600	2.36E-05	12	1.000	0.000
323.400	4.32E-05	14	1.000	0.000
327.700	7.32E-05	16	1.000	0.000
331.700	1.18E-04	18	0.999	0.001
337.400	2.29E-04	20	0.999	0.001
339.000	2.74E-04	22	0.998	0.002
343.400	4.48E-04	24	0.998	0.002
346.900	6.56E-04	26	0.996	0.004
348.800	8.05E-04	28	0.995	0.005
350.800	9.95E-04	30	0.993	0.007
352.600	1.20E-03	32	0.990	0.010
354.500	1.46E-03	34	0.987	0.013
356.400	1.78E-03	36	0.984	0.016
358.100	2.12E-03	38	0.980	0.020
359.700	2.49E-03	40	0.975	0.025
361.200	2.89E-03	42	0.969	0.031
362.600	3.32E-03	44	0.963	0.037
364.200	3.89E-03	46	0.955	0.045
365.900	4.59E-03	48	0.947	0.053
367.600	5.41E-03	50	0.936	0.064
368.500	5.89E-03	52	0.925	0.075
370.100	6.86E-03	54	0.913	0.087
371.400	7.76E-03	56	0.899	0.101
372.000	8.21E-03	58	0.884	0.116
372.300	8.45E-03	60	0.869	0.131
372.500	8.60E-03	62	0.855	0.145
372.400	8.52E-03	64	0.840	0.160
372.300	8.45E-03	66	0.826	0.174
372.300	8.45E-03	68	0.812	0.188
372.200	8.37E-03	70	0.799	0.201
372.000	8.21E-03	72	0.786	0.214
371.700	7.98E-03	74	0.773	0.227
371.400	7.76E-03	76	0.761	0.239
371.200	7.62E-03	78	0.750	0.250
371.000	7.47E-03	80	0.739	0.261
371.600	7.47E-03	82	0.728	0.272
370.600	7.47E-03	84	0.717	0.283
370.300	7.47E-03	86	0.706	0.294
370.200	7.47E-03	88	0.696	0.304
370.100	7.47E-03	90	0.686	0.314
370.100	7.47E-03	90	0.686	0.314
370.300	7.47E-03	92	0.675	0.325
370.500	7.13E-03	94	0.666	0.334
369.700	7.13E-03	96	0.656	0.344
369.500	7.13E-03	98	0.647	0.353
369.400	6.42E-03	100	0.639	0.361
369.400	6.42E-03	102	0.631	0.369
369.400	6.42E-03	104	0.623	0.377
369.500	6.48E-03	106	0.615	0.385
369.500	6.48E-03	108	0.607	0.393
369.600	6.48E-03	110	0.599	0.401
369.600	6.48E-03	112	0.591	0.409
369.700	6.48E-03	114	0.584	0.416
369.800	6.67E-03	116	0.576	0.424
368.900	6.67E-03	118	0.568	0.432
368.900	6.67E-03	120	0.561	0.439
368.900	6.67E-03	122	0.553	0.447
368.700	6.67E-03	124	0.546	0.454
368.700	6.67E-03	126	0.539	0.461
368.700	6.67E-03	128	0.531	0.469
368.700	6.67E-03	130	0.524	0.476
368.600	6.67E-03	132	0.518	0.482
368.600	6.67E-03	134	0.511	0.489
368.600	5.95E-03	136	0.505	0.495
368.600	5.95E-03	138	0.499	0.501
368.600	5.95E-03	140	0.493	0.507
368.600	5.95E-03	142	0.487	0.513
368.600	5.95E-03	144	0.481	0.519
368.600	5.95E-03	146	0.475	0.525
368.600	5.95E-03	148	0.470	0.530
368.600	5.95E-03	150	0.464	0.536
368.600	5.95E-03	152	0.459	0.541
368.600	5.95E-03	154	0.453	0.547
368.600	5.95E-03	156	0.448	0.552
368.600	5.95E-03	158	0.443	0.557
368.600	5.95E-03	160	0.437	0.563
368.600	5.95E-03	162	0.432	0.568
368.600	5.95E-03	164	0.427	0.573
368.600	5.95E-03	166	0.422	0.578
368.600	5.95E-03	168	0.417	0.583
368.600	5.95E-03	170	0.412	0.588
368.600	5.95E-03	172	0.407	0.593
368.600	5.95E-03	174	0.402	0.598
368.600	5.95E-03	176	0.398	0.602

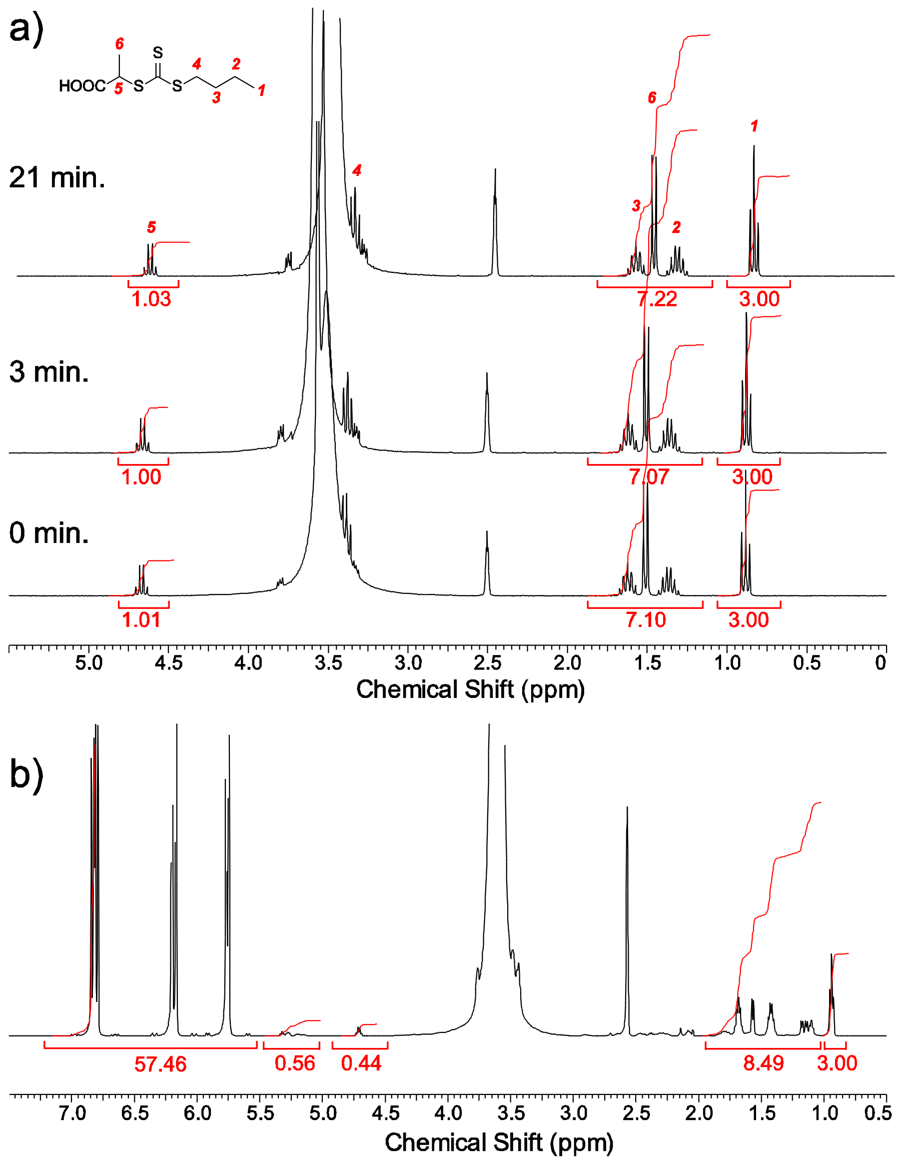

Figure S2. (a) Comparison of the ^{1}H NMR spectra (DMSO-d_6, 300 MHz) of the RAFT agent PABTC after 0, 3, and 21 minutes in a mixture H_2O/dioxane (80/20, *v*/*v*). Peak integration shows no degradation of the CTA. b) ^{1}H NMR spectrum (DMSO-d_6, 300 MHz) of the mixture of NAM and chain transfer agent (without azoinitiator) after 3 min in H_2O/dioxane (80/20, *v*/*v*) at 100˚C in the presence of air and without degassing. Less than 4% of monomer conversion is obtained.

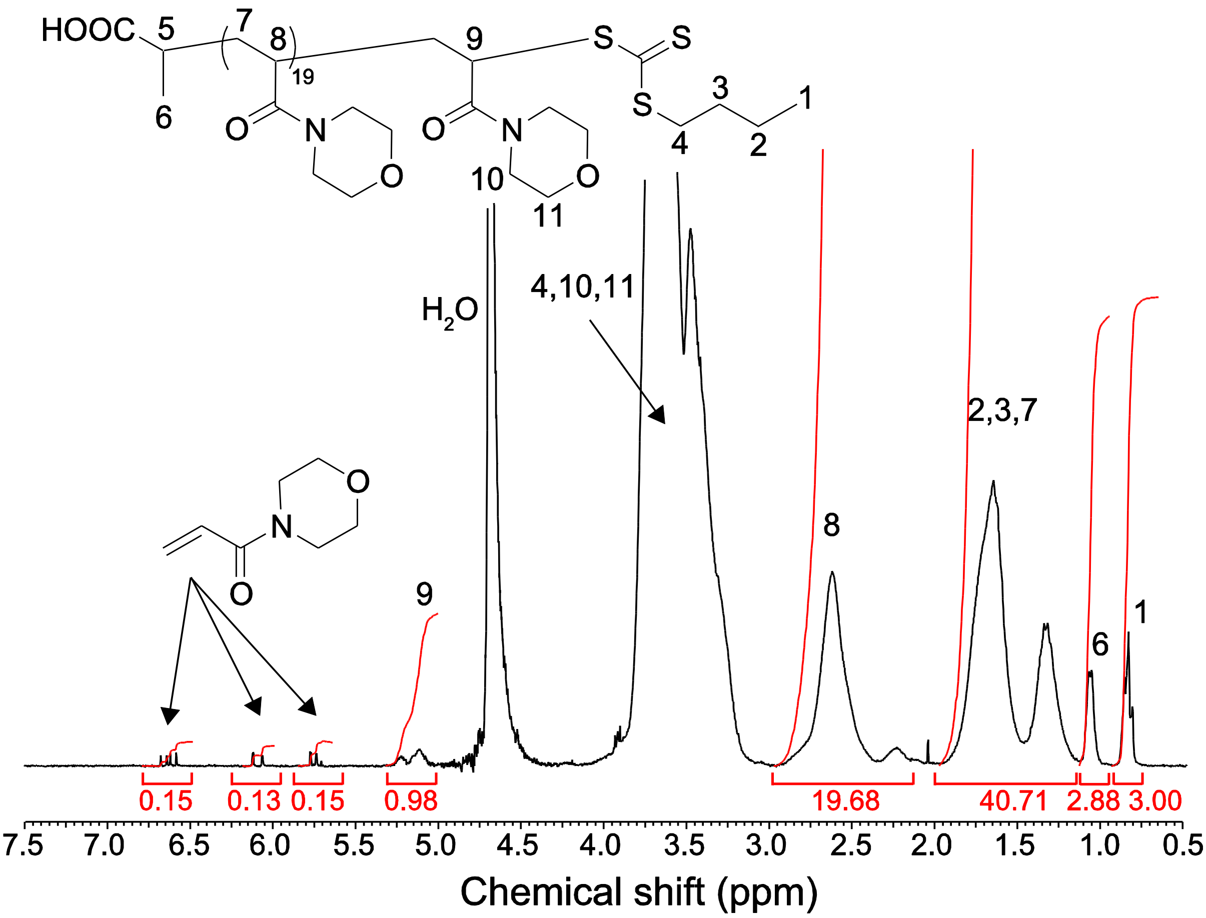

Figure S3. [1]H NMR spectrum (D_2O, 300 MHz) of the polymerization mixture NAM/CTA/VA-044 : 20/1/0.01 (Table S2, cycle 1) after 3 min of RAFT polymerization in H_2O/dioxane (80/20, *v*/*v*) at 100˚C in the presence of air and without degassing (monomer conversion >99%). Comparison of the integrals of 1 with 9 and 6 shows that the CTA does not degrade in the chosen reaction conditions and is fully consumed.

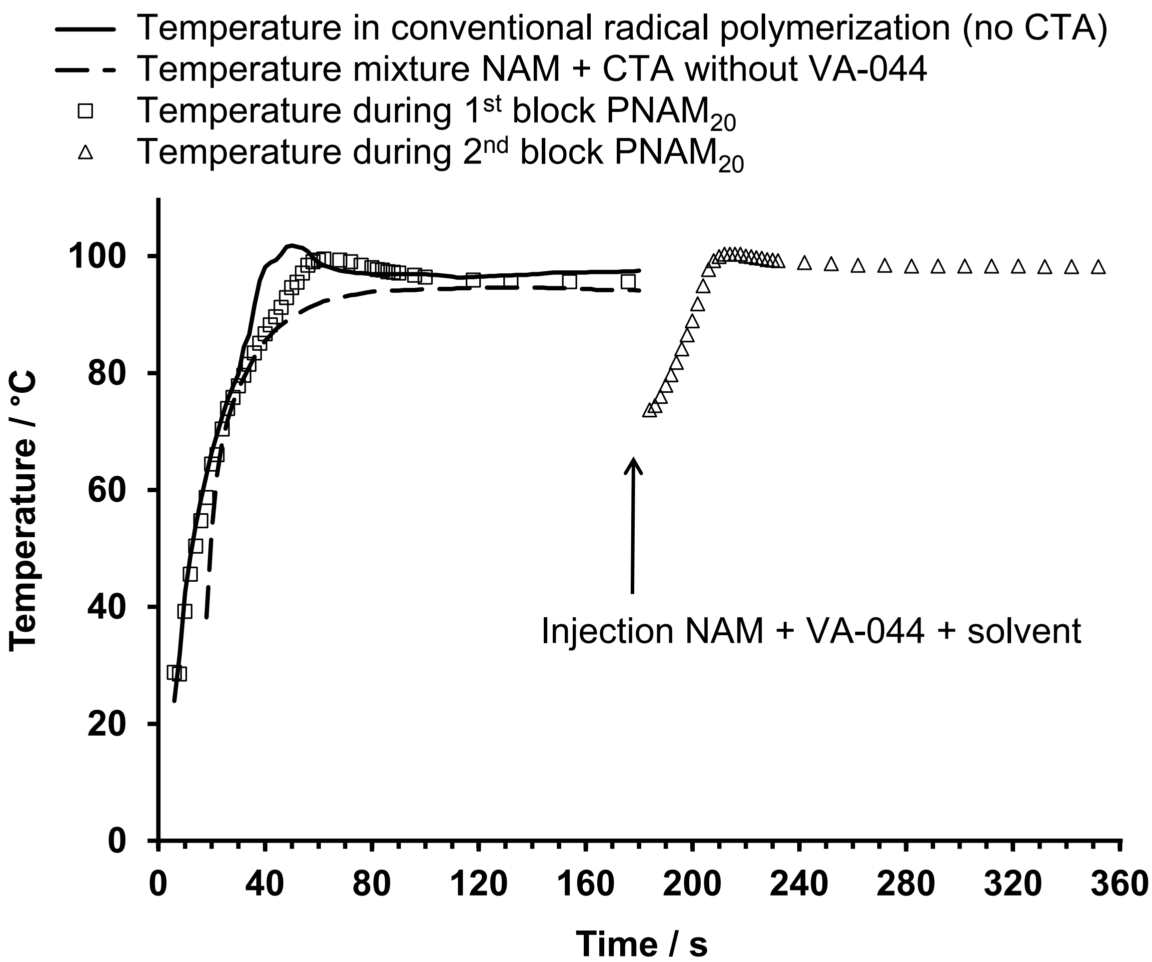

Figure S4. Comparison of the temperature profiles obtained for the NAM homopolymerization by conventional radical polymerization (full line), by RAFT polymerization (empty squares) ($DP_{targeted}$ = 20, see Table S2, cycle 1 for the RAFT polymerization conditions) and for the polymerization mixture without azoinitiator. The $[VA\text{-}044]_0$ used for the conventional radical polymerization is the same than the one in the RAFT process. The temperature profile obtained during the one-pot chain extension with NAM is represented (empty triangles) (see Table S2, cycle 2 for reaction conditions). All the experiments were performed in the presence of air and without degassing.

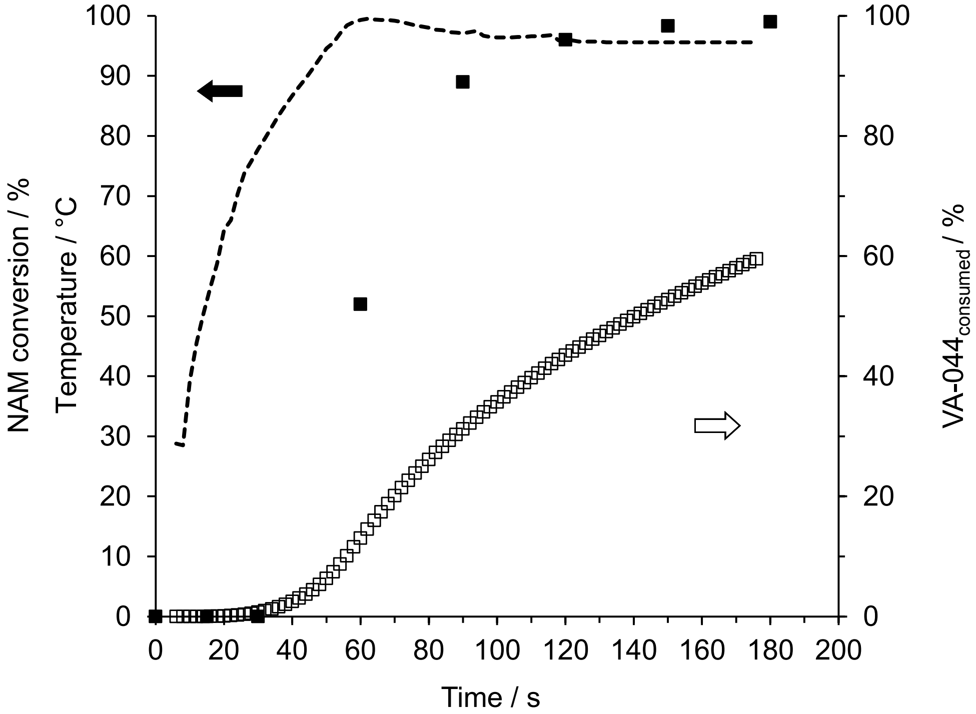

Figure S5. Monomer conversion (full square), percentage of VA-044 consumed (empty square, Equation S1), and temperature (dash line) versus time for the RAFT homopolymerization of NAM in the presence of air and without degassing ($DP_{targeted}$ = 20, see Table S2, cycle 1 for the polymerization conditions).

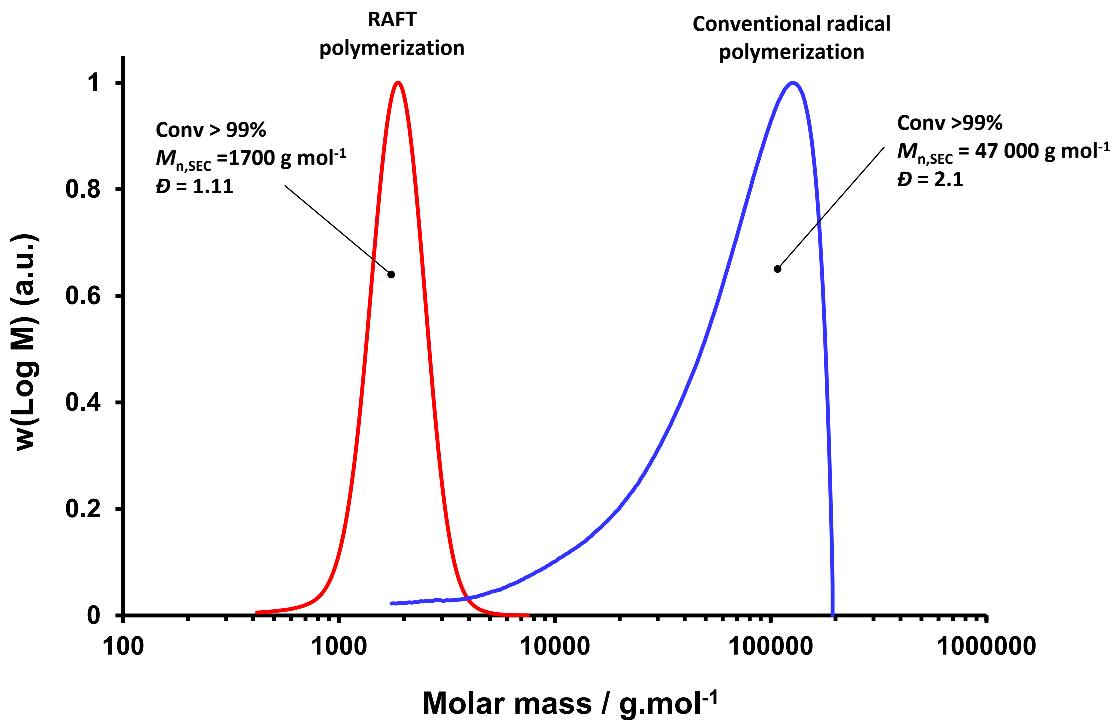

Figure S6. Comparison of the SEC chromatograms of the polymer obtained by conventional radical polymerization of NAM and the $PNAM_{20}$ ($DP_{targeted}$ = 20, Table S2, cycle 1) synthesized by ultrafast RAFT polymerization in the same conditions (H_2O/dioxane : 80/20, *v*/*v* at 100˚C in the presence of air and without degassing). SEC analyses were performed in THF with PSty standards.

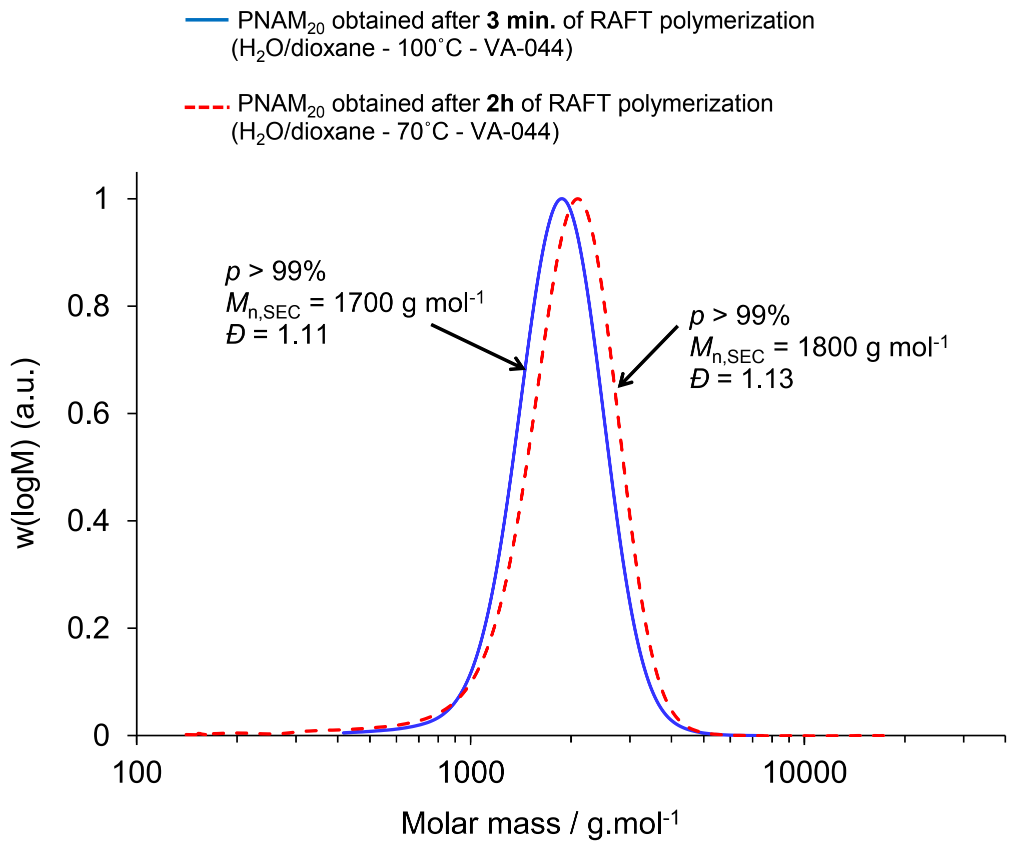

Figure S7. Comparison of the SEC chromatograms of $PNAM_{20}$ synthesized with VA-044 as azoinitiator, in H_2O/dioxane (80/20, *v*/*v*), either at 70˚C under argon for 2 hours or at 100˚C in the presence of air and without degassing for 3 min. SEC analyses were performed on the THF system with PSty standards.

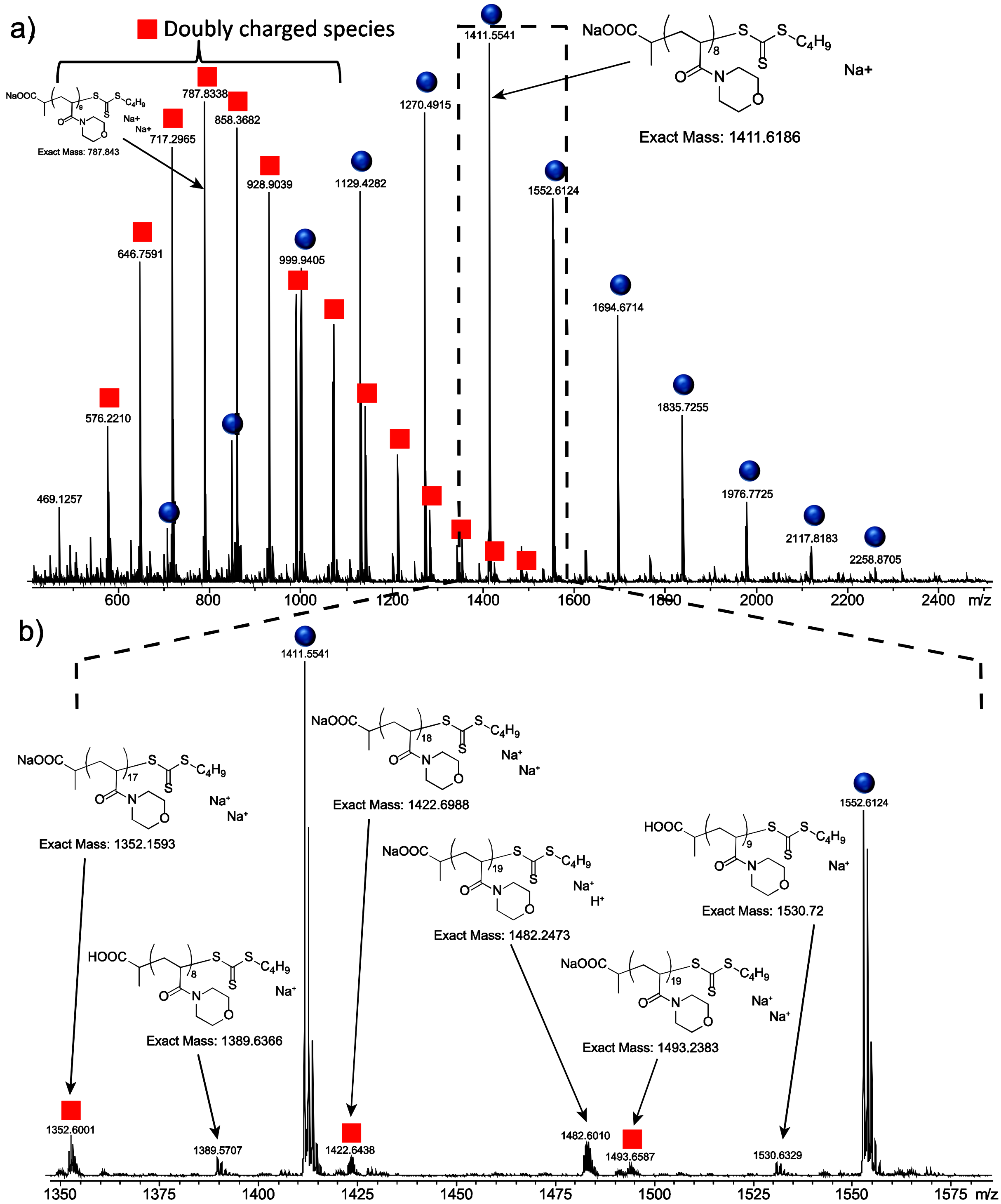

Figure S8. (a) ESI-ToF spectrum and (b) enlargement of the corresponding spectrum showing the excellent retention and stability of the RAFT end-group (no hydrolysis and no degradation) after 3 min of RAFT polymerization performed at 100°C in a mixture dioxane/H_2O (75/25, v/v) in the presence of air and without degassing (i.e., same conditions than the one described in Table S1).

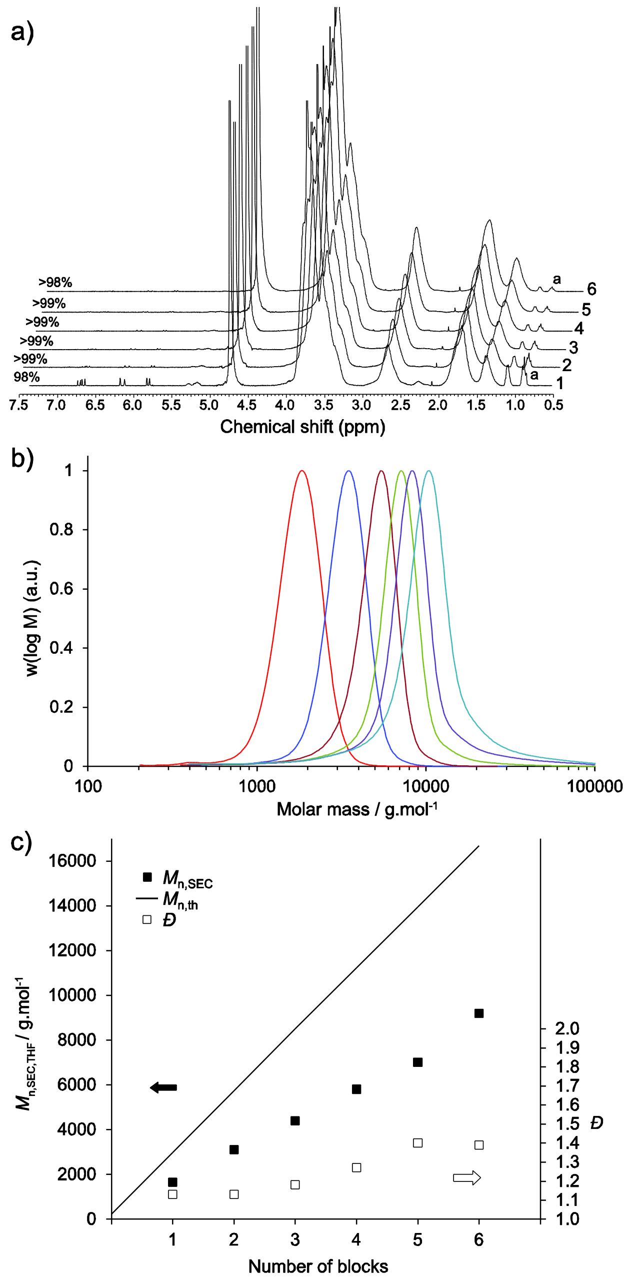

Figure S9. (a) ^{1}H NMR spectra (D_2O, 300 MHz) showing the conversion of NAM for each new block after 3 min of iterative RAFT polymerizations performed in the presence of air and without degassing; (b) SEC chromatograms for successive chain extension of the hexablock $[PNAM_{20}]_6$ (Scheme 3 and Table 1, multiblock **b**) at 100 °C with VA-044 as initiator (3 min per block) (see Table S2 for reaction conditions); (c) Evolution of the number-average molar mass and dispersity with the number of blocks during the preparation of $[PNAM_{20}]_6$. The black line represents the theoretical molar mass calculated from Equation 2. The filled squares represent the experimental molar masses obtained by THF SEC. The empty squares represent the dispersity values as determined by THF SEC.

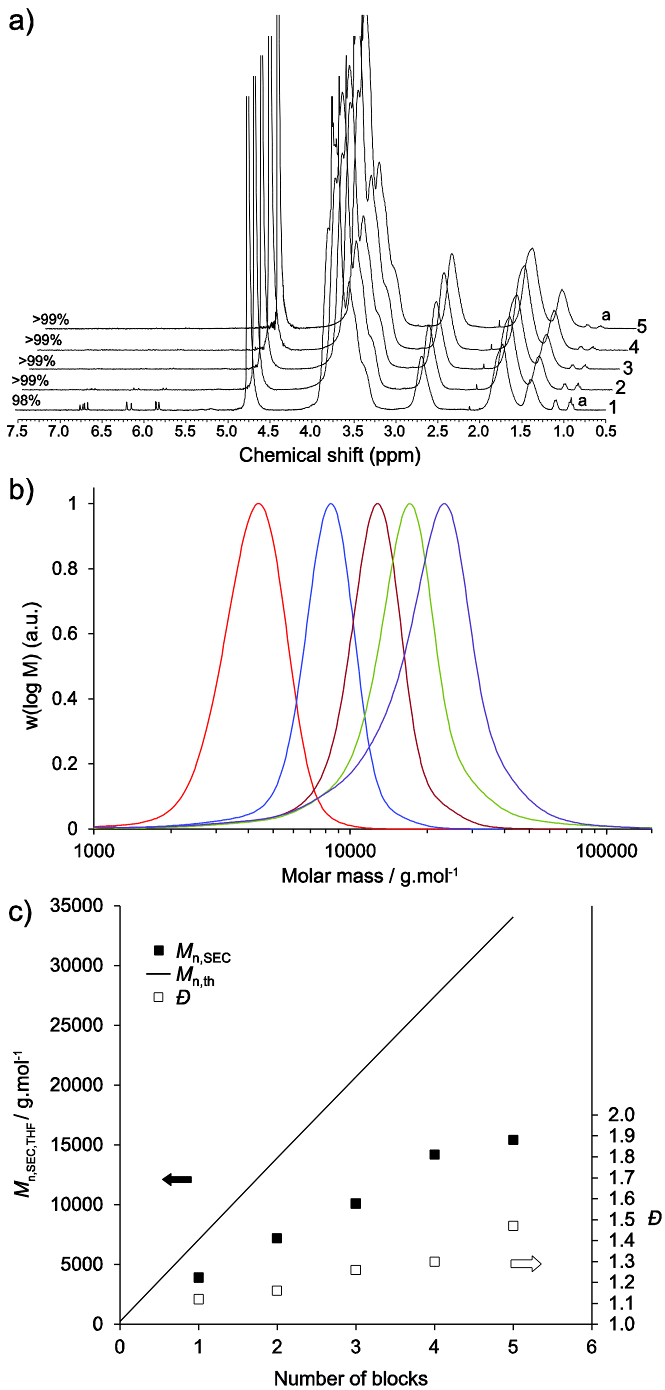

Figure S10. (a) ^{1}H NMR spectra (D_2O, 300 MHz) showing the conversion of NAM for each new block after 3 min of iterative RAFT polymerizations performed in the presence of air and without degassing; (b) SEC chromatograms for successive chain extension of the pentablock $[PNAM_{50}]_5$ (Scheme 3 and Table 1, multiblock **c**) at 100 ˚C with VA-044 as initiator (3 min per block) (see Table S3 for reaction conditions); (c) Evolution of the number-average molar masses and dispersity values with the number of blocks during the preparation of $[PNAM_{50}]_5$. The black line represents the theoretical molar mass calculated from Equation 2. The filled squares represent the experimental molar masses obtained by THF SEC. The empty squares represent the dispersity values as determined by THF SEC.

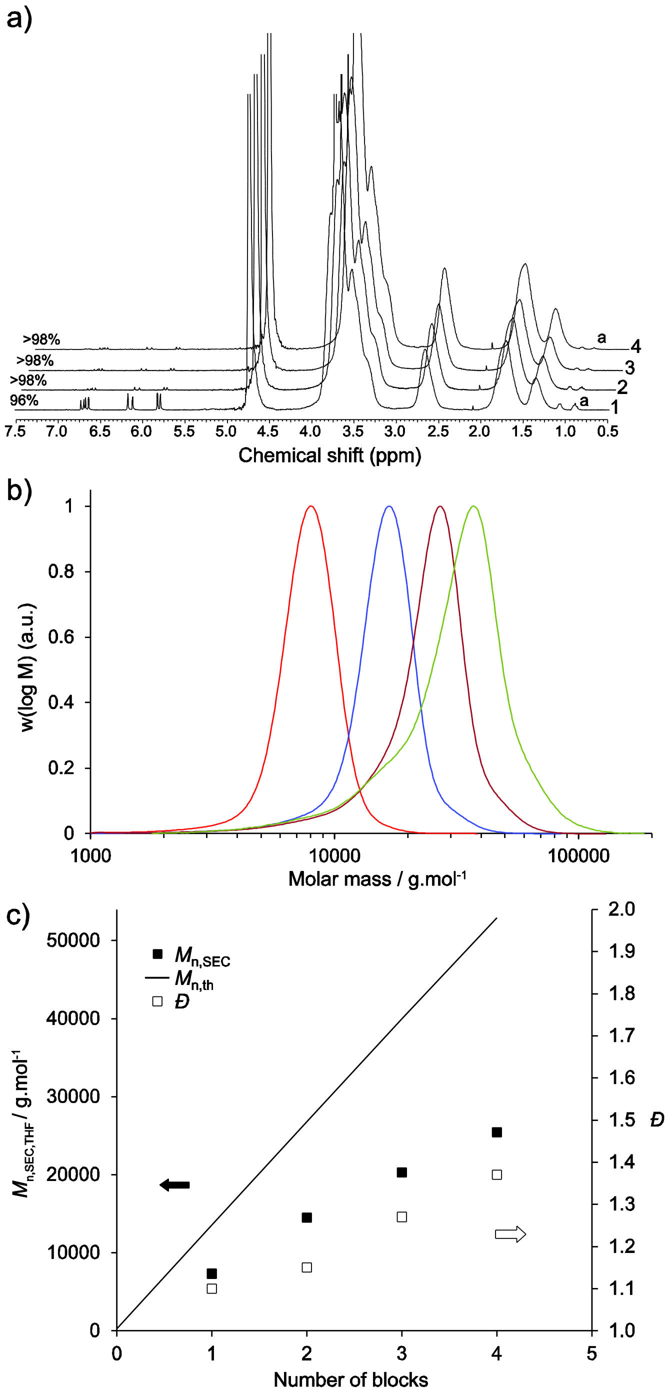

Figure S11. (a) [1]H NMR spectra (D_2O, 300 MHz) showing the conversion of NAM for each new block after 3 min of iterative RAFT polymerizations performed in the presence of air and without degassing; (b) SEC chromatograms for successive chain extension of the tetrablock $[PNAM_{100}]_4$ (Scheme 3 and Table 1, multiblock **d**) at 100°C with VA-044 as initiator (3 min per block) (see Table S4 for reaction conditions); (c) Evolution of the number-average molar masses and dispersity values with the number of blocks during the preparation of $[PNAM_{100}]_4$. The black line represents the theoretical molar mass calculated from Equation 2. The filled squares represent the experimental molar masses obtained by THF SEC. The empty squares represent the dispersity values as determined by THF SEC.

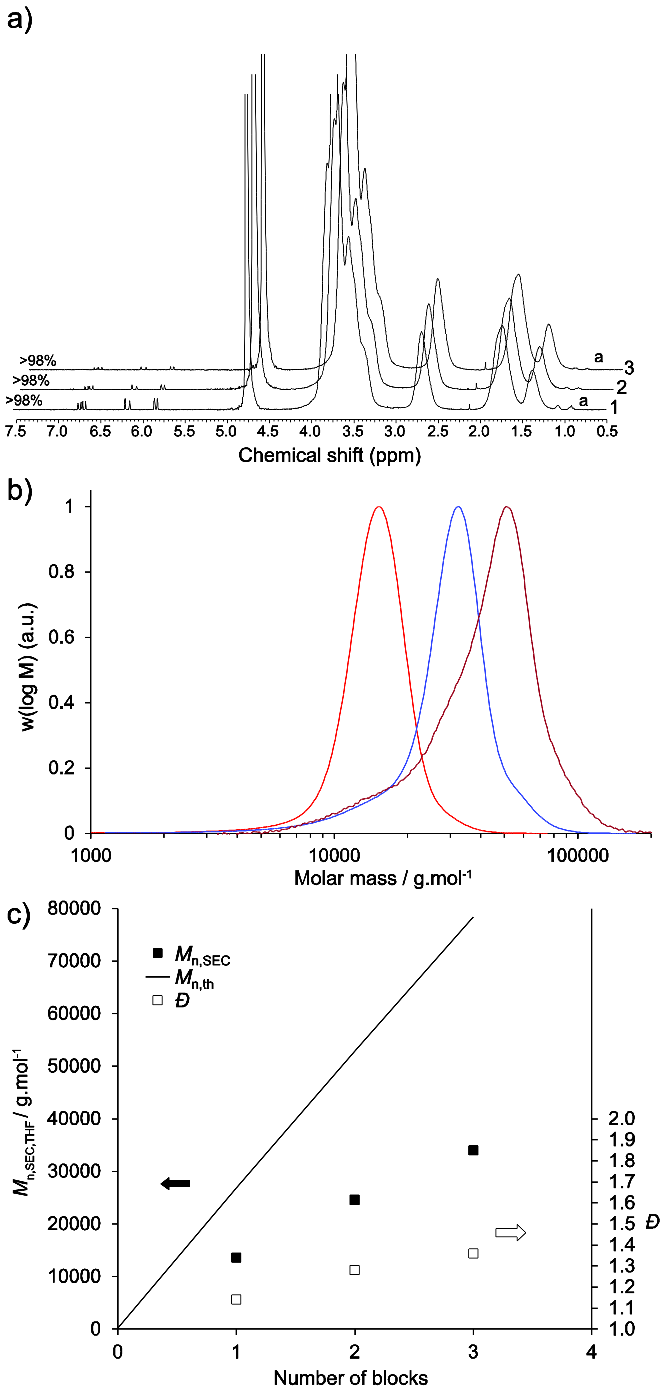

Figure S12. (a) ^{1}H NMR spectra (D_2O, 300 MHz) showing the conversion of NAM for each new block after 3 min of iterative RAFT polymerizations performed in the presence of air and without degassing; (b) SEC chromatograms for successive chain extension of the triblock $[PNAM_{200}]_3$ (Scheme 3 and Table 1, multiblock **e**) at 100˚C with VA-044 as initiator (3 min per block) (see Table S5 for reaction conditions); (c) Evolution of the number-average molar masses and dispersity values with the number of blocks during the preparation of $[PNAM_{200}]_3$. The black line represents the theoretical molar mass calculated from Equation 2. The filled squares represent the experimental molar masses obtained by THF SEC. The empty squares represent the dispersity values as determined by THF SEC.

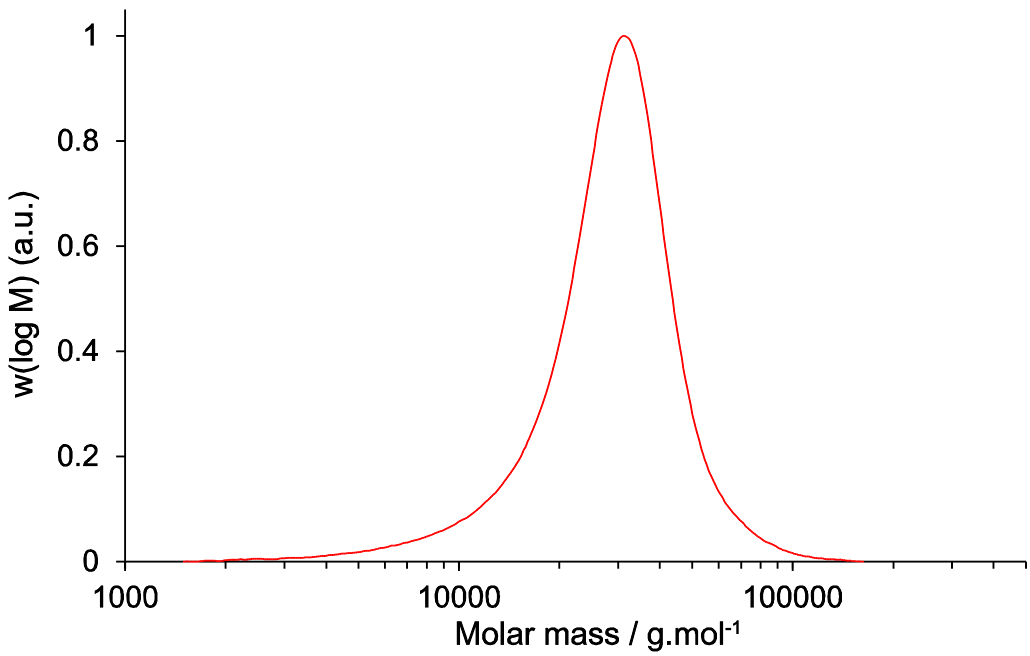

Figure S13. SEC chromatogram of the homopolymer $PNAM_{400}$ (Scheme 3 and Table 1, homopolymer **f**) synthesized by RAFT polymerization at 100˚C with VA-044 as initiator (3 min per block), in the presence of air and without degassing. SEC was performed on the THF system. Refer to Table S6 for exact reaction conditions.

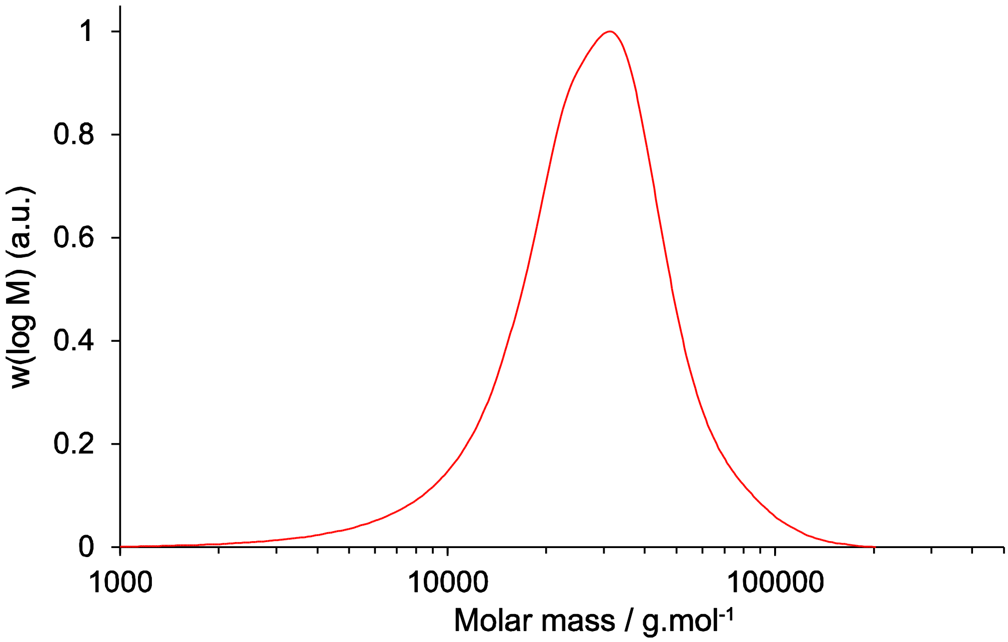

Figure S14. SEC chromatogram of the homopolymer $PNAM_{600}$ (Scheme 3 and Table 1, homopolymer **g**) synthesized by RAFT polymerization at 100˚C with VA-044 as initiator (3 min per block), in the presence of air and without degassing. SEC was performed on the THF system. Refer to Table S7 for exact reaction conditions.

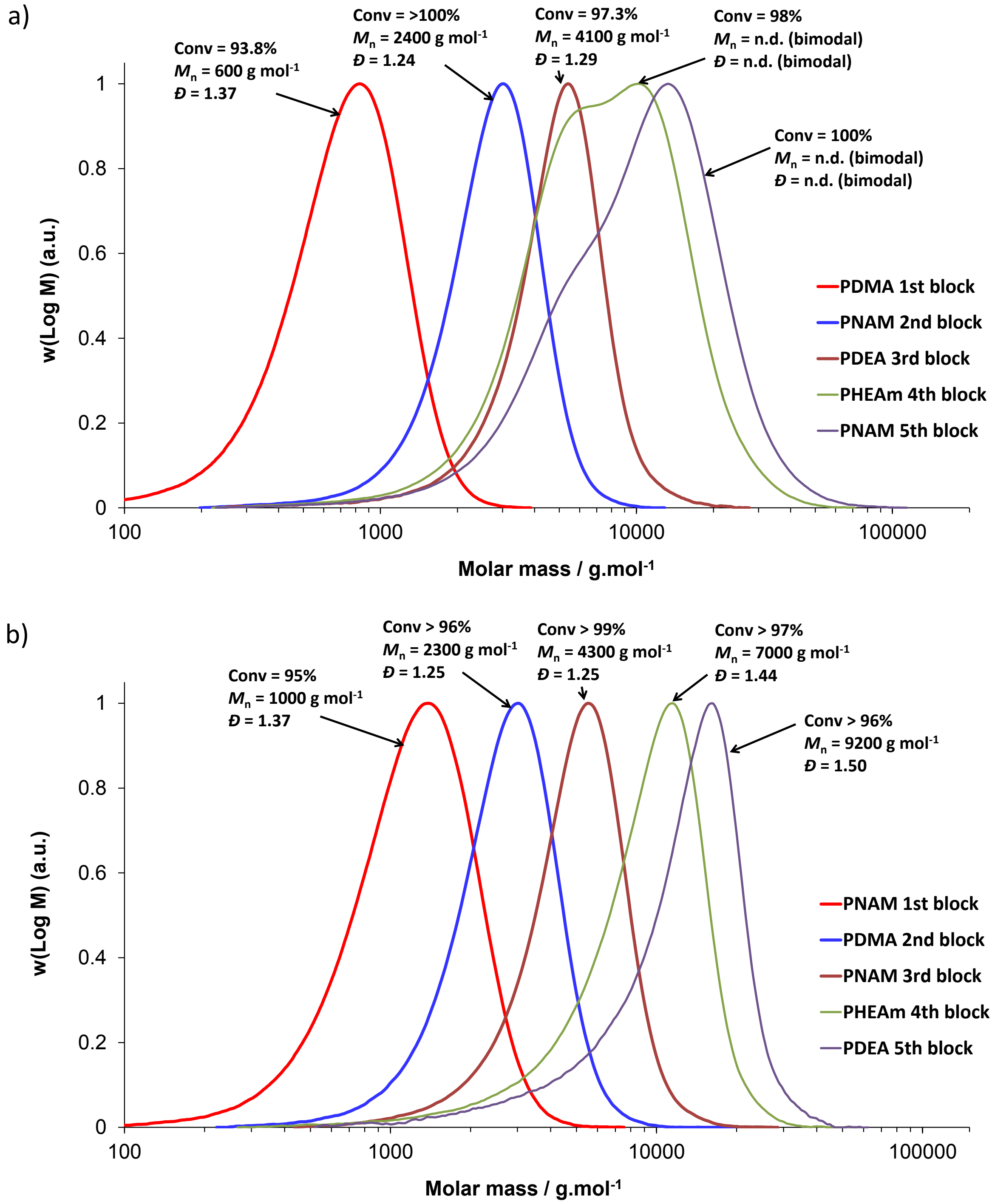

Figure S15. Comparison of the SEC chromatograms of the two pentablock copolymers (a) $PNAM_{20}$-*b*-$PDMA_{20}$-*b*-**$PDEA_{20}$**-*b*-$PHEAm_{20}$-*b*-$PNAM_{20}$ and (b) $PNAM_{20}$-*b*-$PDMA_{20}$-*b*-$PNAM_{20}$-*b*-$PHEAm_{20}$-*b*-**$PDEA_{20}$** showing the impact of having the thermoresponsive block $PDEA_{20}$ ~~at~~ as the 3rd block or as the final 5th block. Both multiblock copolymers have been prepared in similar condition (see Table S8) at 100˚C with VA-044 as initiator (3 min per block) in the presence of air and without degassing. SEC analyses were performed on the DMF system with PMMA standards.

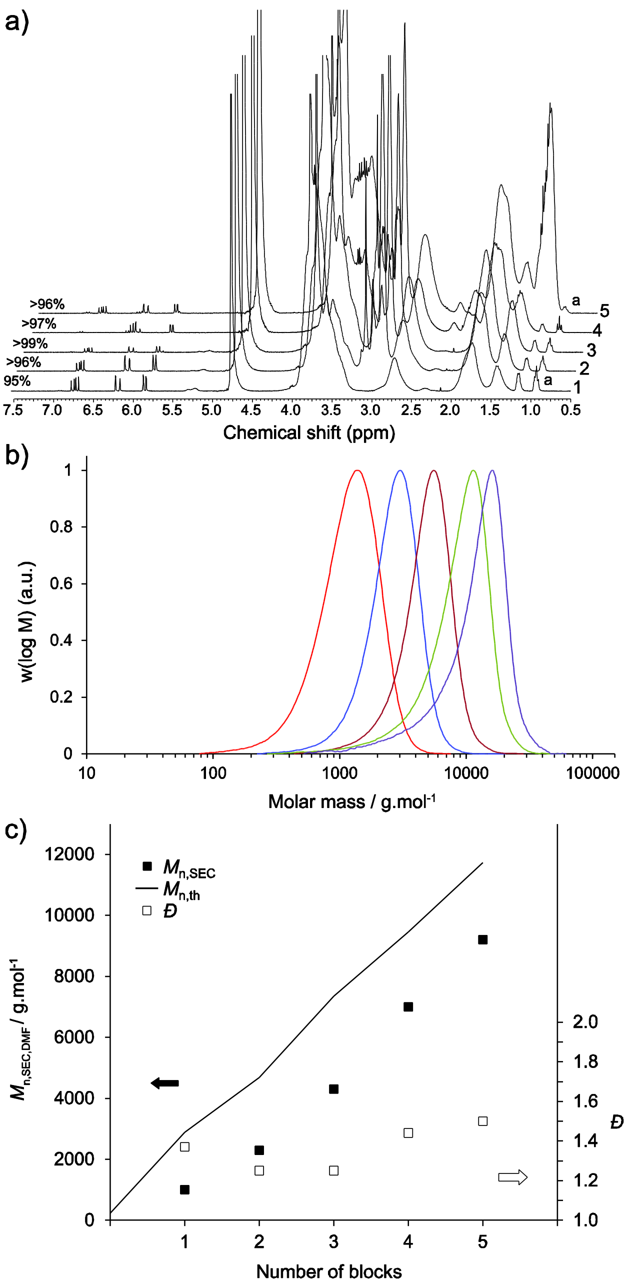

Figure S16. (a) [1]H NMR spectra (D_2O, 300 MHz) showing the monomer conversion for each block after 3 min of iterative RAFT polymerization in the presence of air and without degassing; (b) SEC chromatograms for successive block extensions of the pentablock $PNAM_{20}$-*b*-$PDMA_{20}$-*b*-$PNAM_{20}$-*b*-$PHEAm_{20}$-*b*-$PDEA_{20}$ (Scheme 4 and Table 2, multiblock **i**) at 100˚C with VA-044 as initiator (3 min per block) (see Table S9 for reaction conditions); (c) Evolution of the number-average molar mass and dispersity with the number of blocks during the preparation of the pentablock copolymer. The black line represents the theoretical molar mass calculated from Equation 2. The filled squares represent the experimental molar masses obtained by DMF SEC. The empty squares represent the dispersity values as determined by DMF SEC.

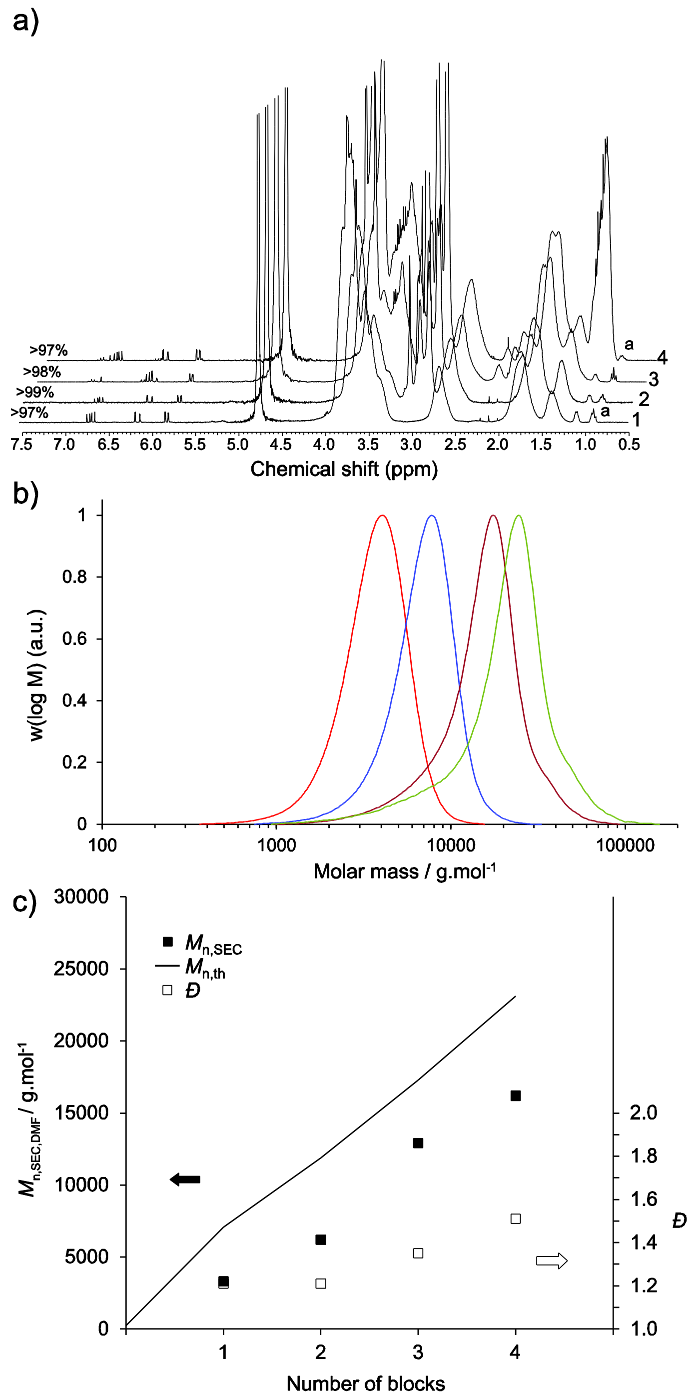

Figure S17. (a) [1]H NMR spectra (D_2O, 300 MHz) showing the monomer conversion for each block after 3 min of iterative RAFT polymerization in the presence of air and without degassing; (b) MWDs for successive block extensions of the tetrablock $PNAM_{50}$-*b*-$PDMA_{50}$-*b*-$PHEAm_{50}$-*b*-$PDEA_{50}$ (Scheme 4 and Table 2, multiblock **j**) at 100°C with VA-044 as initiator (3 min per block) (see Table S10 for reaction conditions); (c) Evolution of the number-average molar mass and dispersity with the number of blocks during the preparation of the tetrablock copolymer. The black line represents the theoretical molar mass calculated from Equation 2. The filled squares represent the experimental molar masses obtained by DMF SEC. The empty squares represent the dispersity values as determined by DMF SEC.

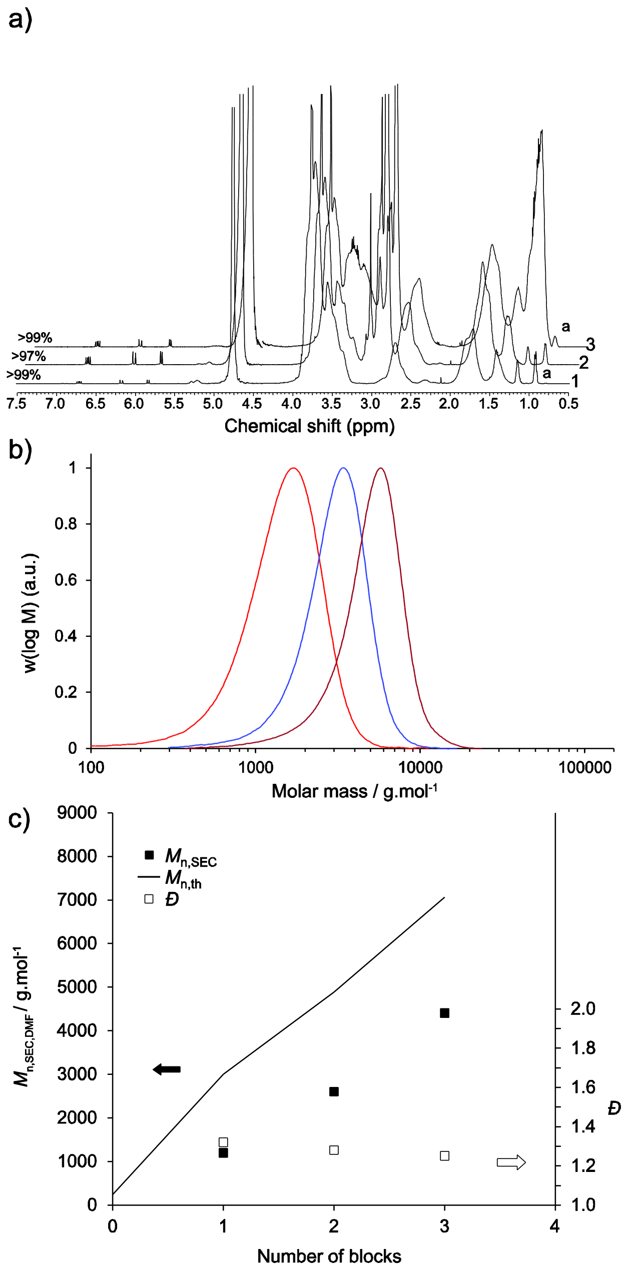

Figure S18. (a) [1]H NMR spectra (D_2O, 300 MHz) showing the monomer conversion for each block after 3 min of iterative RAFT polymerization in the presence of air and without degassing; (b) MWDs for successive block extensions of the triblock PNAM$_{20}$-*b*-PDMA$_{20}$-*b*-PHEAm$_{20}$ (Scheme 4 and Table 2, multiblock **k**) at 100˚C with VA-044 as initiator (3 min per block) (see Table S11 for reaction conditions); (c) Evolution of the number-average molar mass and dispersity with the number of blocks during the preparation of the triblock copolymer. The black line represents the theoretical molar mass calculated from Equation 2. The filled squares represent the experimental molar masses obtained by DMF SEC. The empty squares represent the dispersity values as determined by DMF SEC.

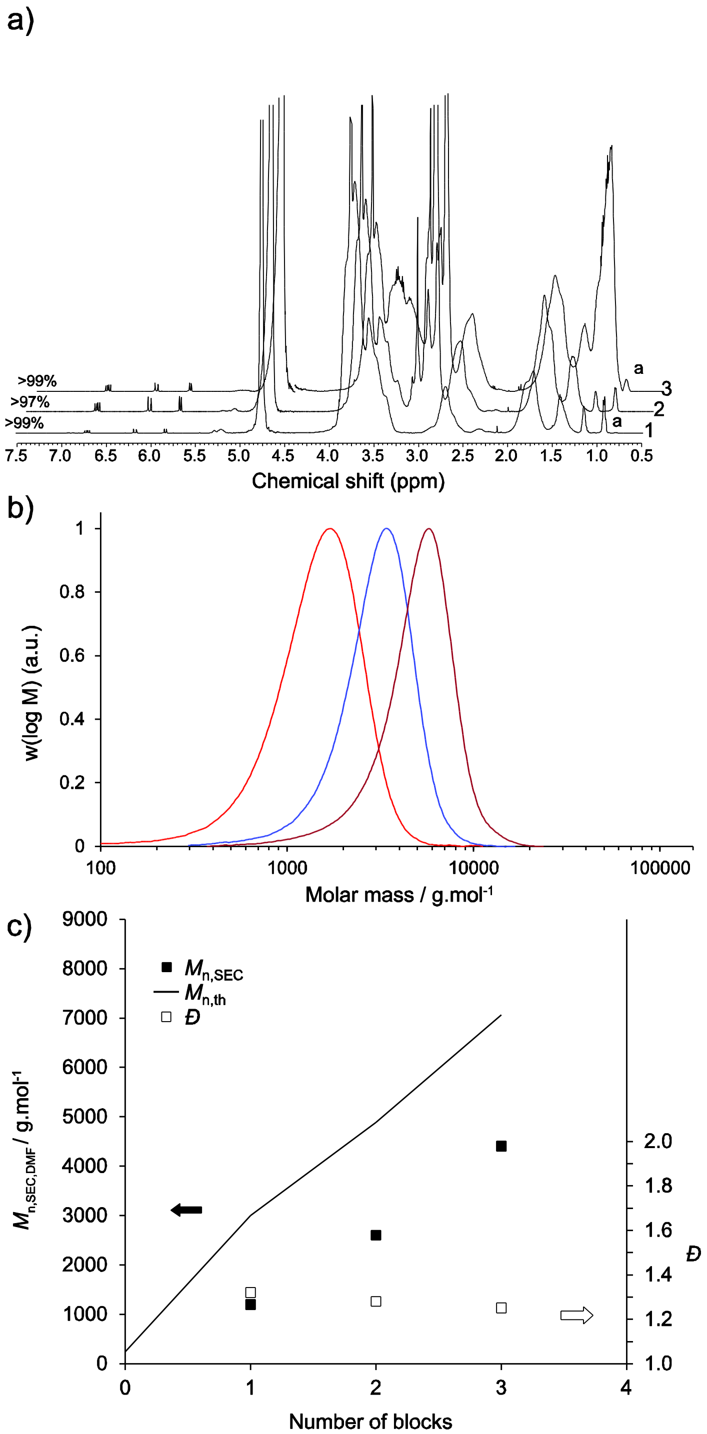

Figure S19. (a) ^{1}H NMR spectra (D_2O, 300 MHz) showing the monomer conversion for each block after 3 min of iterative RAFT polymerization in the presence of air and without degassing; (b) MWDs for successive block extensions of the triblock $PNAM_{20}$-*b*-$PDMA_{20}$-*b*-$PDEA_{20}$ (Scheme 4 and Table 2, multiblock **I**) at 100°C with VA-044 as initiator (3 min. per block) (see Table S12 for reaction conditions); (c) Evolution of the number-average molar mass and dispersity with the number of blocks during the preparation of the triblock copolymer. The black line represents the theoretical molar mass calculated from Equation 2. The filled squares represent the experimental molar masses obtained by DMF SEC. The empty squares represent the dispersity values as determined by DMF SEC.

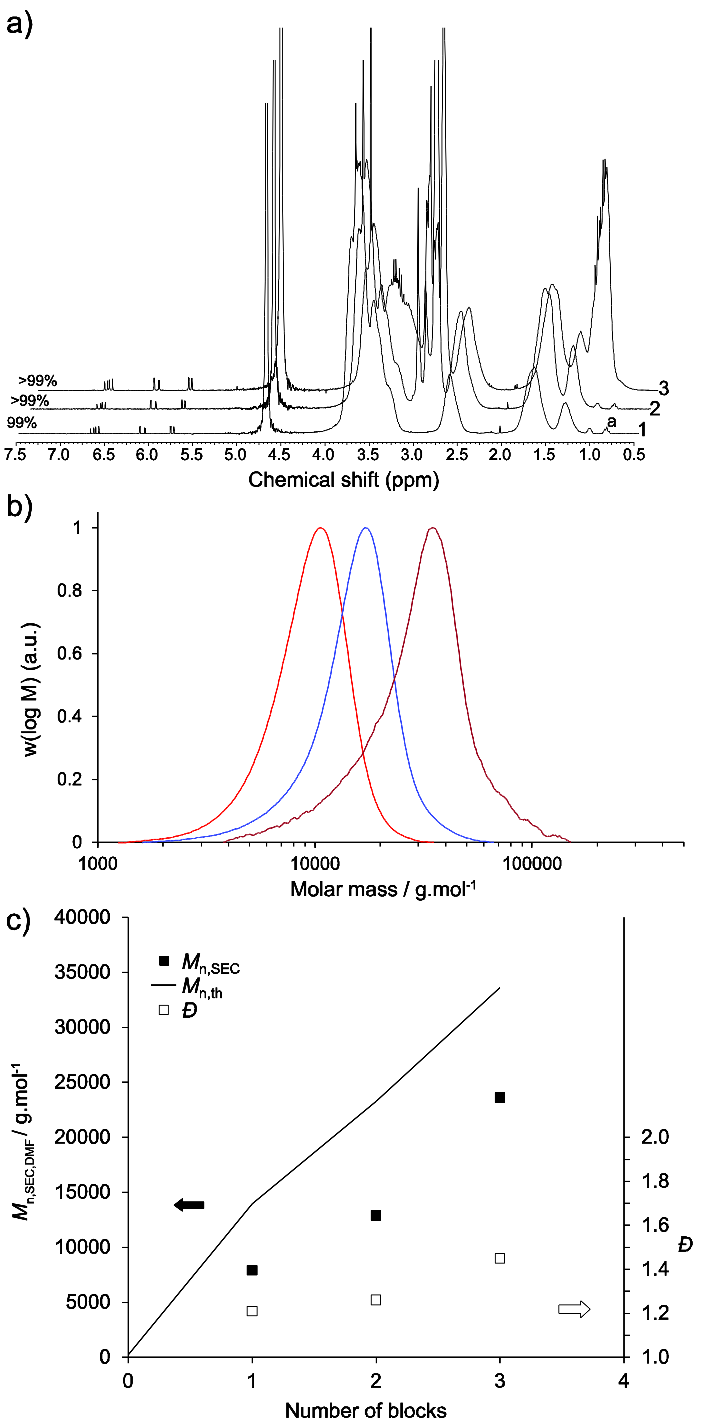

Figure S20. (a) ^{1}H NMR spectra (D_2O, 300 MHz) showing the monomer conversion for each block after 3 min of iterative RAFT polymerization in the presence of air and without degassing; (b) MWDs for successive block extensions of the triblock $PNAM_{100}$-*b*-$PDMA_{100}$-*b*-$PDEA_{100}$ (Scheme 4 and Table 2, multiblock **m**) at 100°C with VA-044 as initiator (3 min per block) (see Table S13 for reaction conditions); (c) Evolution of the number-average molar mass and dispersity with the number of blocks during the preparation of the triblock copolymer. The black line represents the theoretical molar mass calculated from Equation 2. The filled squares represent the experimental molar masses obtained by DMF SEC. The empty squares represent the dispersity values as determined by DMF SEC.

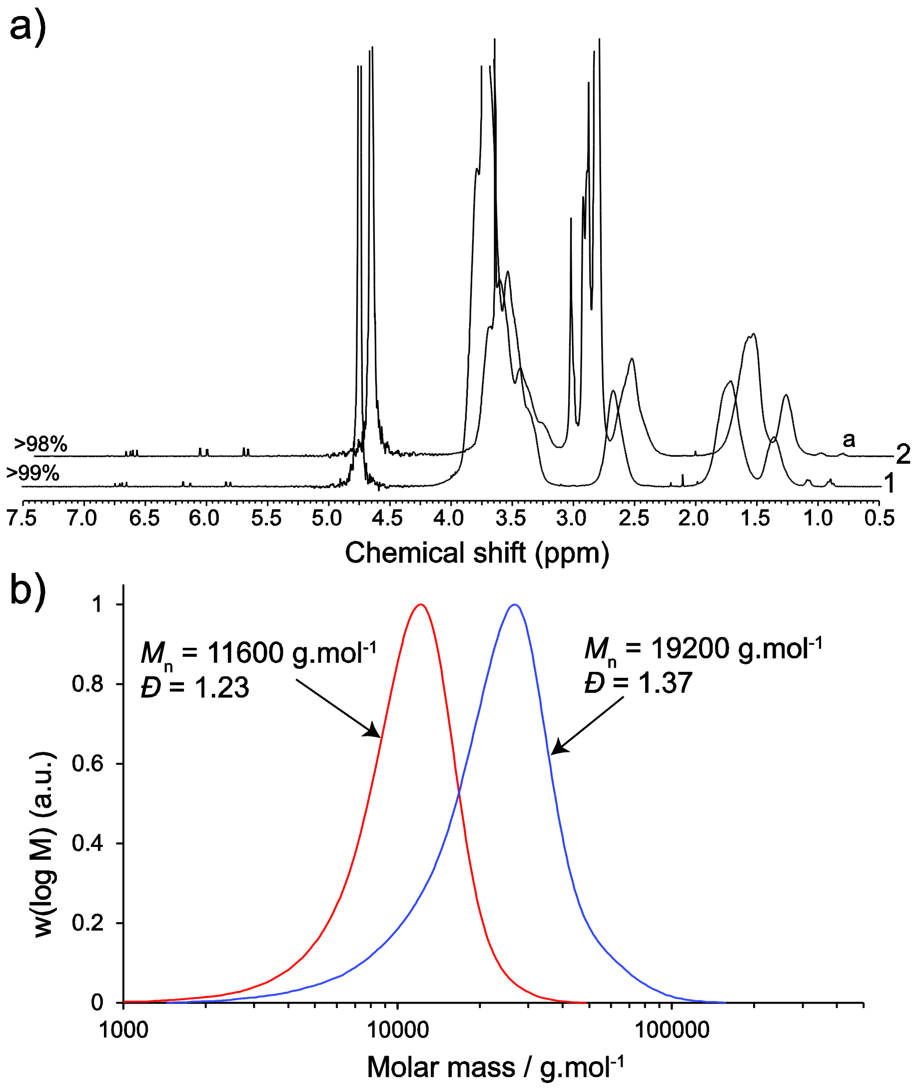

Figure S21. (a) ^{1}H NMR spectra (D_2O, 300 MHz) showing the monomer conversion for each block after 3 min of iterative RAFT polymerization in the presence of air and without degassing; (b) SEC chromatograms for successive block extensions of the diblock $PNAM_{150}$-*b*-$PDMA_{150}$ (Scheme 4 and Table 2, multiblock **n**) at 100°C with VA-044 as initiator (3 min per block) (see Table S14 for reaction conditions), as well as number-average molar masses and dispersity values for the different blocks as determined with the DMF SEC system.

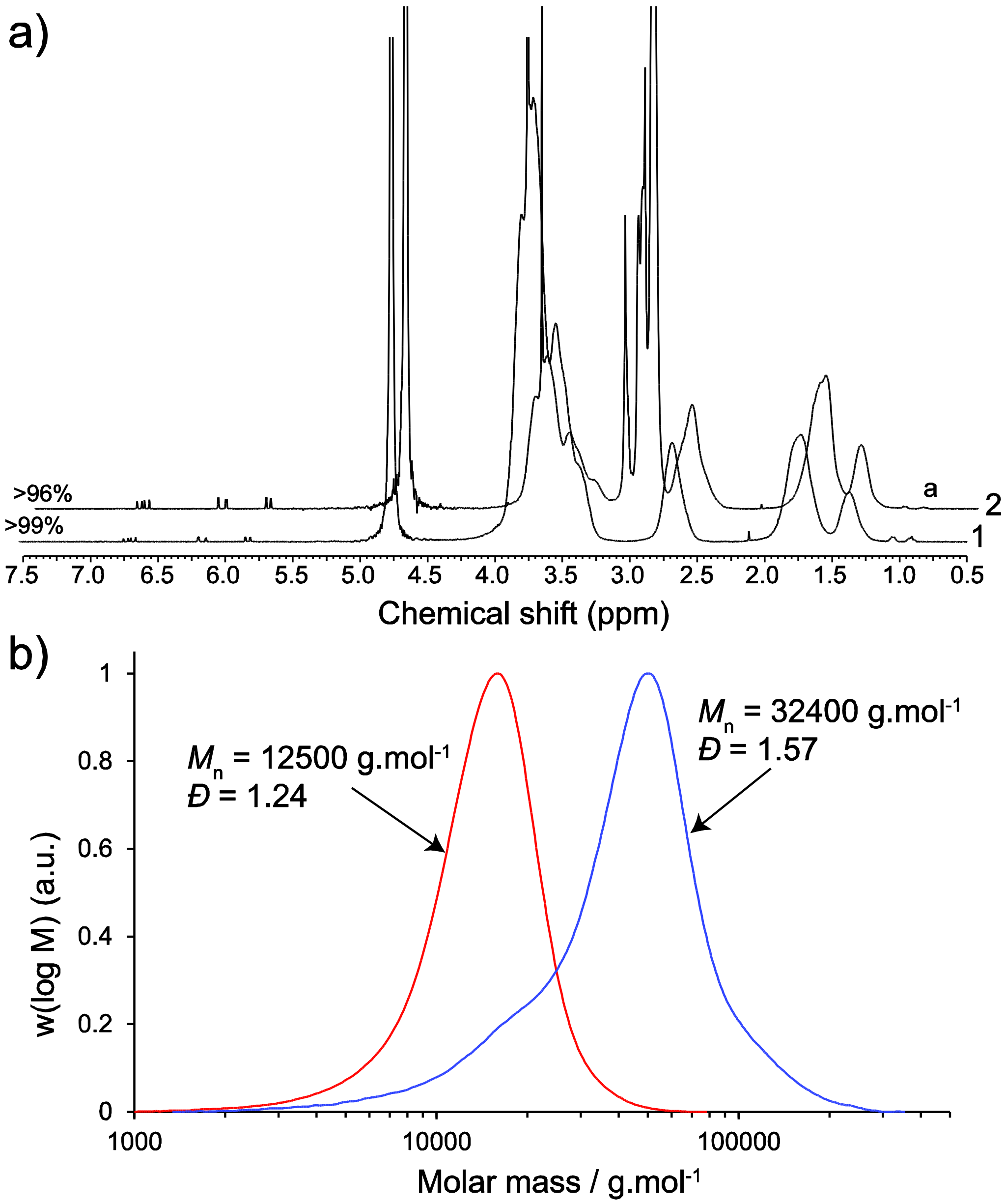

Figure S22. (a) ^{1}H NMR spectra (D_2O, 300 MHz) showing the monomer conversion for each block after 3 min of iterative RAFT polymerization in the presence of air and without degassing; (b) SEC chromatograms for successive block extensions of the diblock copolymer PNAM$_{200}$-*b*-PDMA$_{200}$ (Scheme 4 and Table 2, multiblock **o**) at 100˚C with VA-044 as initiator (3 min per block) (see Table S15 for reaction conditions), as well as number-average molar masses and dispersity values for the different blocks as determined with the DMF SEC system.

Table S1. Experimental conditions for the preparation of the heptablock $[PNAM_{10}]_7$ (Scheme 3, multiblock **a**) in H_2O/dioxane at 100˚C with VA-044 as initiator (3 min per block, in the presence of air, and without degassing).

Cycles	1	2	3	4	5	6	7
Monomer	NAM	NAM	NAM	NAM	NAM	NAM	NAM
$DP_{targeted}$	10	10	10	10	10	10	10
$m_{monomer\ added}$ (mg)	400	400	400	400	400	400	400
$m_{CTA\ added}$ (mg)	67.6	-	-	-	-	-	-
$m_{VA\text{-}044\ added}$ (mg)	0.611	0.458	0.705	0.916	1.145	1.409	1.666
$m_{VA\text{-}044\ initial}$ [a] (mg)	0.611	0.702	0.902	1.168	1.472	1.821	2.176
$V_{H2O\ added}$ (mL)	0.264	0.352	0.352	0.352	0.352	0.352	0.352
$V_{dioxane\ added}$ (mL)	0.088	-	-	-	-	-	-
% H_2O	75.0	87.5	91.7	93.7	95.0	95.8	96.4
V_{total} [b] (mL)	0.709	1.417	2.125	2.834	3.542	4.250	4.959
$[VA\text{-}044]_0$ (mol.L^{-1})	2.7 10^{-3}	1.5 10^{-3}	1.3 10^{-3}	1.3 10^{-3}	1.3 10^{-3}	1.3 10^{-3}	1.4 10^{-3}
$[NAM]_0$ (mol.L^{-1})	4.00	2.00	1.33	1.00	0.80	0.67	0.57
$[CTA]_0/[VA\text{-}044]_0$	150	130	102	78	62	50	42
L [c] (%)	99.6	99.5	99.3	99.1	98.9	98.6	98.3
Cumulative L [d] (%)	99.6	99.1	98.4	97.5	96.3	95.0	93.4

[a] $m_{VA\text{-}044\ initial}$ represents the sum of the initiator added $m_{VA\text{-}044\ added}$ + the amount of initiator remaining from the previous block. [b] represents the sum of the volume of the solvent added + volume of the monomer added + V_{total} previous block; [c] theoretical estimation of the fraction of living chains per block (e.g. extendable chains having the Z group); [d] theoretical estimation of the cumulated fraction of living chains

Table S2. Experimental conditions for the preparation of the hexablock $[PNAM_{20}]_6$ (Scheme 3, multiblock **b**) in H_2O/dioxane at 100°C with VA-044 as initiator (3 min per block, in the presence of air, and without degassing).

Cycles	1	2	3	4	5	6
Monomer	NAM	NAM	NAM	NAM	NAM	NAM
$DP_{targeted}$	20	20	20	20	20	20
$m_{monomer\ added}$ (mg)	400	400	400	400	400	400
$m_{CTA\ added}$ (mg)	33.8	-	-	-	-	-
$m_{VA\text{-}044\ added}$ (mg)	0.458	0.458	0.705	0.916	1.145	1.309
$m_{VA\text{-}044\ initial}$ [a] (mg)	0.458	0.641	0.885	1.164	1.471	1.721
$V_{H2O\ added}$ (mL)	0.282	0.352	0.352	0.352	0.352	0.352
$V_{dioxane\ added}$ (mL)	0.070	-	-	-	-	-
% H_2O	80.1	90.0	93.4	95.0	96.0	96.7
V_{total} [b] (mL)	0.708	1.416	2.125	2.833	3.541	4.250
$[VA\text{-}044]_0$ (mol.L^{-1})	2.0 10^{-3}	1.4 10^{-3}	1.3 10^{-3}	1.3 10^{-3}	1.3 10^{-3}	1.2 10^{-3}
$[NAM]_0$ (mol.L^{-1})	4.00	2.00	1.33	1.00	0.80	0.67
$[CTA]_0$/[$VA\text{-}044]_0$	100	71	52	39	31	27
L [c] (%)	99.4	99.0	98.6	98.2	97.7	97.4
Cumulative L [d] (%)	99.4	98.4	97.1	95.3	93.2	90.7

[a] $m_{VA\text{-}044\ initial}$ represents the sum of the initiator added $m_{VA\text{-}044\ added}$ + the amount of initiator remaining from the previous block. [b] represents the sum of the volume of the solvent added + volume of the monomer added + V_{total} previous block; [c] theoretical estimation of the fraction of living chains per block (e.g. extendable chains having the Z group); [d] theoretical estimation of the cumulated fraction of living chains

Table S3. Experimental conditions for the preparation of the pentablock $[PNAM_{50}]_5$ (Scheme 3, multiblock **c**) in H_2O/dioxane at 100°C with VA-044 as initiator (3 min per block, in the presence of air, and without degassing).

Cycles	1	2	3	4	5
Monomer	NAM	NAM	NAM	NAM	NAM
$DP_{targeted}$	50	50	50	50	50
$m_{monomer\ added}$ (mg)	400	400	400	400	400
$m_{CTA\ added}$ (mg)	13.5	-	-	-	-
$m_{VA\text{-}044\ added}$ (mg)	0.229	0.366	0.555	0.733	0.916
$m_{VA\text{-}044\ initial}$ [a] (mg)	0.229	0.458	0.683	0.924	1.175
$V_{H2O\ added}$ (mL)	0.317	0.352	0.352	0.352	0.352
$V_{dioxane\ added}$ (mL)	0.035	-	-	-	-
% H_2O	80.1	90.0	93.4	95.0	96.0
V_{total} [b] (mL)	0.708	1.417	2.125	2.833	3.542
$[VA\text{-}044]_0$ ($mol.L^{-1}$)	$1.0\ 10^{-3}$	$1.0\ 10^{-3}$	$9.9\ 10^{-4}$	$1.0\ 10^{-3}$	$1.0\ 10^{-3}$
$[NAM]_0$ ($mol.L^{-1}$)	4.00	2.00	1.33	1.00	0.80
$[CTA]_0/[VA\text{-}044]_0$	80	40	27	20	16
L [c] (%)	99.3	98.2	97.4	96.5	95.6
Cumulative L [d] (%)	99.3	97.5	95.0	91.6	87.6

[a] $m_{VA\text{-}044\ initial}$ represents the sum of the initiator added $m_{VA\text{-}044\ added}$ + the amount of initiator remaining from the previous block. [b] represents the sum of the volume of the solvent added + volume of the monomer added + V_{total} previous block; [c] theoretical estimation of the fraction of living chains per block (e.g. extendable chains having the Z group); [d] theoretical estimation of the cumulated fraction of living chains

Table S4. Experimental conditions for the preparation of the tetrablock $[PNAM_{100}]_4$ (Scheme 3, multiblock **d**) in H_2O/dioxane at 100˚C with VA-044 as initiator (3 min per block, in the presence of air, and without degassing).

Cycles	1	2	3	4
Monomer	NAM	NAM	NAM	NAM
$DP_{targeted}$	100	100	100	100
$m_{monomer\ added}$ (mg)	400	400	400	400
$m_{CTA\ added}$ (mg)	6.7	-	-	-
$m_{VA\text{-}044\ added}$ (mg)	0.183	0.395	0.458	0.611
$m_{VA\text{-}044\ initial}$ [a] (mg)	0.183	0.468	0.589	0.776
$V_{H2O\ added}$ (mL)	0.430	0.566	0.453	0.352
$V_{dioxane\ added}$ (mL)	0.023	-	-	-
% H_2O	94.9	97.7	98.4	98.7
V_{total} [b] (mL)	0.810	1.733	2.542	3.352
$[VA\text{-}044]_0$ (mol.L^{-1})	7.0 10^{-4}	8.4 10^{-4}	7.2 10^{-4}	7.2 10^{-4}
$[NAM]_0$ (mol.L^{-1})	3.50	1.64	1.11	0.85
$[CTA]_0/[VA\text{-}044]_0$	50	20	16	12
L [c] (%)	98.8	96.5	95.6	94.3
Cumulative L [d] (%)	98.8	95.3	91.1	85.9

[a] $m_{VA\text{-}044\ initial}$ represents the sum of the initiator added $m_{VA\text{-}044\ added}$ + the amount of initiator remaining from the previous block. [b] represents the sum of the volume of the solvent added + volume of the monomer added + V_{total} previous block; [c] theoretical estimation of the fraction of living chains per block (e.g. extendable chains having the Z group); [d] theoretical estimation of the cumulated fraction of living chains

Table S5. Experimental conditions for the preparation of the triblock $[PNAM_{200}]_3$ (Scheme 3, multiblock **e**) in H_2O/dioxane at 100˚C with VA-044 as initiator (3 min per block, in the presence of air, and without degassing).

Cycles	1	2	3
Monomer	NAM	NAM	NAM
$DP_{targeted}$	200	200	200
$m_{monomer\ added}$ (mg)	400	400	400
$m_{CTA\ added}$ (mg)	3.4	-	-
$m_{VA\text{-}044\ added}$ (mg)	0.183	0.278	0.398
$m_{VA\text{-}044\ initial}$ [a] (mg)	0.183	0.351	0.496
$V_{H2O\ added}$ (mL)	0.430	0.453	0.453
$V_{dioxane\ added}$ (mL)	0.023	-	-
% H_2O	94.9	97.5	98.3
V_{total} [b] (mL)	0.810	1.619	2.429
$[VA\text{-}044]_0$ ($mol.L^{-1}$)	$7.0\ 10^{-4}$	$6.7\ 10^{-4}$	$6.3\ 10^{-4}$
$[NAM]_0$ ($mol.L^{-1}$)	3.50	1.75	1.17
$[CTA]_0/[VA\text{-}044]_0$	25	13	9
L [c] (%)	97.7	94.8	92.8
Cumulative L [d] (%)	97.7	92.5	85.8

[a] $m_{VA\text{-}044\ initial}$ represents the sum of the initiator added $m_{VA\text{-}044\ added}$ + the amount of initiator remaining from the previous block. [b] represents the sum of the volume of the solvent added + volume of the monomer added + V_{total} previous block; [c] theoretical estimation of the fraction of living chains per block (e.g. extendable chains having the Z group); [d] theoretical estimation of the cumulated fraction of living chains

Table S6. Experimental conditions for the preparation of $PNAM_{400}$ (Scheme 3, multiblock **f**) in H_2O/dioxane at 100˚C with VA-044 as initiator (3 min polymerization, in the presence of air, and without degassing).

Cycles	1
Monomer	NAM
$DP_{targeted}$	400
$m_{monomer\ added}$ (mg)	500
$m_{CTA\ added}$ (mg)	2.1
$m_{VA\text{-}044\ added}$ (mg)	0.191
$V_{H2O\ added}$ (mL)	0.671
$V_{dioxane\ added}$ (mL)	0.037
% H_2O	95.0
V_{total} (mL)	1.181
$[VA\text{-}044]_0$ ($mol.L^{-1}$)	$5\ 10^{-4}$
$[NAM]_0$ ($mol.L^{-1}$)	3
$[CTA]_0/[VA\text{-}044]_0$	15
L [a] (%)	95.5

[a] theoretical estimation of the fraction of living chains per block (e.g. extendable chains having the Z group).

Table S7. Experimental conditions for the preparation of $PNAM_{600}$ (Scheme 3, multiblock **g**) in H_2O/dioxane at 100˚C with VA-044 as initiator (3 min polymerization, in the presence of air, and without degassing).

Cycles	1
Monomer	NAM
$DP_{targeted}$	600
$m_{monomer\ added}$ (mg)	500
$m_{CTA\ added}$ (mg)	1.4
$m_{VA\text{-}044\ added}$ (mg)	0.191
$V_{H2O\ added}$ (mL)	0.671
$V_{dioxane\ added}$ (mL)	0.037
% H_2O	95.0
V_{total} (mL)	1.181
$[VA\text{-}044]_0$ ($mol.L^{-1}$)	$5\ 10^{-4}$
$[NAM]_0$ ($mol.L^{-1}$)	3
$[CTA]_0/[VA\text{-}044]_0$	10
L [a] (%)	93.5

[a] theoretical estimation of the fraction of living chains per block (e.g. extendable chains having the Z group).

Table S8. Experimental conditions for the preparation of the pentablock copolymer $PNAM_{10}$-*b*-$PDMA_{10}$-*b*-$PNAM_{10}$-*b*-$PHEAm_{10}$-*b*-$PDEA_{10}$ (Scheme 4, multiblock **h**) in H_2O/dioxane at 100°C with VA-044 as initiator (3 min per block, in the presence of air, and without degassing).

Cycles	1	2	3	4	5
Monomer	NAM	DMA	NAM	HEAm	DEA
$DP_{targeted}$	10	10	10	10	10
$m_{monomer\ added}$ (mg)	400	281	400	326	360
$m_{CTA\ added}$ (mg)	67.6				
$m_{VA\text{-}044\ added}$ (mg)	0.611	0.573	0.763	1.145	1.527
$m_{VA\text{-}044\ initial}$ [a] (mg)	0.611	0.817	0.992	1.423	1.925
V_{H2O} (mL)	0.264	0.220	0.317	0.273	0.319
$V_{dioxane\ added}$ (mL)	0.088	0.055	0.035	0.000	0.000
% H_2O	75.0	84.6	90.1	92.4	94.1
V_{total} [b] (mL)	0.708	1.275	1.983	2.550	3.258
$[VA\text{-}044]_0$ ($mol.L^{-1}$)	2.7 10^{-3}	2.0 10^{-3}	1.6 10^{-3}	1.7 10^{-3}	1.8 10^{-3}
$[M]_0$ ($mol.L^{-1}$)	4.00	2.22	1.43	1.11	0.87
$[CTA]_0/[VA\text{-}044]_0$	150	112	92	64	48
L[c] (%)	99.6	99.4	99.2	98.9	98.5
Cumulative L[d] (%)	99.6	99.0	98.2	97.1	95.7

[a] $m_{VA\text{-}044\ initial}$ represents the sum of the initiator added $m_{VA\text{-}044\ added}$ + the amount of initiator remaining from the previous block. [b] represents the sum of the volume of the solvent added + volume of the monomer added + V_{total} previous block; [c] theoretical estimation of the fraction of living chains per block (e.g. extendable chains having the Z group); [d] theoretical estimation of the cumulated fraction of living chains

Table S9. Experimental conditions for the preparation of the pentablock copolymer $PNAM_{20}$-*b*-$PDMA_{20}$-*b*-$PNAM_{20}$-*b*-$PHEAm_{20}$-*b*-$PDEA_{20}$ (Scheme 4, multiblock **i**) in H_2O/dioxane at 100˚C with VA-044 as initiator (3 min per block, in the presence of air, and without degassing).

Cycles	1	2	3	4	5
Monomer	NAM	DMA	NAM	HEAm	DEA
$DP_{targeted}$	20	20	20	20	20
$m_{monomer\ added}$ (mg)	400	281	400	326	360
$m_{CTA\ added}$ (mg)	33.8				
$m_{VA\text{-}044\ added}$ (mg)	0.458	0.458	0.611	1.018	1.145
$m_{VA\text{-}044\ initial}$ [a] (mg)	0.458	0.641	0.791	1.239	1.492
V_{H2O} (mL)	0.264	0.220	0.317	0.273	0.319
$V_{dioxane\ added}$ (mL)	0.088	0.055	0.035	0.000	0.000
% H_2O	75.0	84.6	90.1	92.4	94.1
V_{total} [b] (mL)	0.708	1.275	1.983	2.550	3.258
$[VA\text{-}044]_0$ ($mol.L^{-1}$)	$2.0\ 10^{-3}$	$1.6\ 10^{-3}$	$1.2\ 10^{-3}$	$1.5\ 10^{-3}$	$1.4\ 10^{-3}$
$[M]_0$ ($mol.L^{-1}$)	4.00	2.22	1.43	1.11	0.87
$[CTA]_0/[VA\text{-}044]_0$	100	71	58	37	31
L[c] (%)	99.4	99.0	98.8	98.1	97.7
Cumulative L[d] (%)	99.4	98.4	97.2	95.4	93.2

[a] $m_{VA\text{-}044\ initial}$ represents the sum of the initiator added $m_{VA\text{-}044\ added}$ + the amount of initiator remaining from the previous block. [b] represents the sum of the volume of the solvent added + volume of the monomer added + V_{total} previous block; [c] theoretical estimation of the fraction of living chains per block (e.g. extendable chains having the Z group); [d] theoretical estimation of the cumulated fraction of living chains

Table S10. Experimental conditions for the preparation of the tetrablock copolymer $PNAM_{50}$-*b*-$PDMA_{50}$-*b*-$PHEAm_{50}$-*b*-$PDEA_{50}$ (Scheme 4, multiblock **j**) in H_2O/dioxane at 100°C with VA-044 as initiator (3 min per block, in the presence of air, and without degassing).

Cycles	1	2	3	4
Monomer	NAM	DMA	HEAm	DEA
$DP_{targeted}$	50	50	50	50
$m_{monomer\ added}$ (mg)	400	281	326	360
$m_{CTA\ added}$ (mg)	13.5			
$m_{VA\text{-}044\ added}$ (mg)	0.229	0.366	0.611	0.833
$m_{VA\text{-}044\ initial}$ [a] (mg)	0.229	0.458	0.739	1.040
V_{H2O} (mL)	0.362	0.179	0.218	0.319
$V_{dioxane\ added}$ (mL)	0.091	0.045	0.055	0.000
% H_2O	79.9	85.6	89.3	92.2
V_{total} [b] (mL)	0.810	1.325	1.893	2.601
$[VA\text{-}044]_0$ ($mol.L^{-1}$)	$8.8\ 10^{-4}$	$1.1\ 10^{-3}$	$1.2\ 10^{-3}$	$1.2\ 10^{-3}$
$[M]_0$ ($mol.L^{-1}$)	3.50	2.14	1.50	1.09
$[CTA]_0/[VA\text{-}044]_0$	80	40	25	18
L[c] (%)	99.3	98.2	97.2	96.1
Cumulative L[d] (%)	99.3	97.5	94.8	91.0

[a] $m_{VA\text{-}044\ initial}$ represents the sum of the initiator added $m_{VA\text{-}044\ added}$ + the amount of initiator remaining from the previous block. [b] represents the sum of the volume of the solvent added + volume of the monomer added + V_{total} previous block; [c] theoretical estimation of the fraction of living chains per block (e.g. extendable chains having the Z group); [d] theoretical estimation of the cumulated fraction of living chains

Table S11. Experimental conditions for the preparation of the triblock copolymer $PNAM_{20}$-*b*-$PDMA_{20}$-*b*-$PDEA_{20}$ (Scheme 4, multiblock **k**) in H_2O/dioxane at 100°C with VA-044 as initiator (3 min per block, in the presence of air, and without degassing).

Cycles	1	2	3
Monomer	NAM	DMA	DEA
$DP_{targeted}$	20	20	20
$m_{monomer\ added}$ (mg)	500	351	450
$m_{CTA\ added}$ (mg)	42.2		
$m_{VA\text{-}044\ added}$ (mg)	0.716	0.573	0.881
$m_{VA\text{-}044\ initial}$ [a] (mg)	0.716	0.859	1.122
V_{H2O} (mL)	0.425	0.225	0.376
$V_{dioxane\ added}$ (mL)	0.142	0	0
% H_2O	74.9	82.1	87.8
V_{total} [b] (mL)	1.012	1.603	2.466
$[VA\text{-}044]_0$ ($mol.L^{-1}$)	$2.2\ 10^{-3}$	$1.7\ 10^{-3}$	$1.4\ 10^{-3}$
$[M]_0$ ($mol.L^{-1}$)	3.50	2.21	1.44
$[CTA]_0/[VA\text{-}044]_0$	80	67	51
L[c] (%)	99.3	98.9	98.6
Cumulative L[d] (%)	99.3	98.2	96.8

[a] $m_{VA\text{-}044\ initial}$ represents the sum of the initiator added $m_{VA\text{-}044\ added}$ + the amount of initiator remaining from the previous block. [b] represents the sum of the volume of the solvent added + volume of the monomer added + V_{total} previous block; [c] theoretical estimation of the fraction of living chains per block (e.g. extendable chains having the Z group); [d] theoretical estimation of the cumulated fraction of living chains

Table S12. Experimental conditions for the preparation of the triblock copolymer $PNAM_{20}$-*b*-$PDMA_{20}$-*b*-$PHEAm_{20}$ (Scheme 4, multiblock **I**) in H_2O/dioxane at 100˚C with VA-044 as initiator (3 min per block, in the presence of air, and without degassing).

Cycles	1	2	3
Monomer	NAM	DMA	HEAm
$DP_{targeted}$	20	20	20
$m_{monomer\ added}$ (mg)	500	351	408
$m_{CTA\ added}$ (mg)	42.2		
$m_{VA\text{-}044\ added}$ (mg)	0.716	0.498	0.881
$m_{VA\text{-}044\ initial}$ [a] (mg)	0.716	0.784	1.101
V_{H2O} (mL)	0.425	0.334	0.814
$V_{dioxane\ added}$ (mL)	0.142	0	0
% H_2O	74.9	84.4	91.8
V_{total} [b] (mL)	1.012	1.721	2.902
$[VA\text{-}044]_0$ ($mol.L^{-1}$)	$2.2\ 10^{-3}$	$1.4\ 10^{-3}$	$1.2\ 10^{-3}$
$[M]_0$ ($mol.L^{-1}$)	3.50	2.06	1.22
$[CTA]_0/[VA\text{-}044]_0$	80	73	52
L[c] (%)	99.3	99.0	98.6
Cumulative L[d] (%)	99.3	98.3	96.9

[a] $m_{VA\text{-}044\ initial}$ represents the sum of the initiator added $m_{VA\text{-}044\ added}$ + the amount of initiator remaining from the previous block. [b] represents the sum of the volume of the solvent added + volume of the monomer added + V_{total} previous block; [c] theoretical estimation of the fraction of living chains per block (e.g. extendable chains having the Z group); [d] theoretical estimation of the cumulated fraction of living chains

Table S13. Experimental conditions for the preparation of the triblock copolymer $PNAM_{100}$-*b*-$PDMA_{100}$-*b*-$PDEA_{100}$ (Scheme 4, multiblock **m**) in H_2O/dioxane at 100˚C with VA-044 as initiator (3 min per block, in the presence of air, and without degassing).

Cycles	1	2	3
Monomer	NAM	DMA	DEA
$DP_{targeted}$	100	100	100
$m_{monomer\ added}$ (mg)	500	351	450
$m_{CTA\ added}$ (mg)	8.4		
$m_{VA\text{-}044\ added}$ (mg)	0.229	0.382	0.674
$m_{VA\text{-}044\ initial}$ [a] (mg)	0.229	0.474	0.807
V_{H2O} (mL)	0.538	0.225	0.221
$V_{dioxane\ added}$ (mL)	0.028	0	0
% H_2O	95.1	96.5	97.2
V_{total} [b] (mL)	1.012	1.602	2.310
$[VA\text{-}044]_0$ ($mol.L^{-1}$)	$7.0\ 10^{-4}$	$9.1\ 10^{-4}$	$1.1\ 10^{-3}$
$[M]_0$ ($mol.L^{-1}$)	3.50	2.21	1.53
$[CTA]_0/[VA\text{-}044]_0$	50	24	14
L[c] (%)	98.8	97.1	95.2
Cumulative L[d] (%)	98.8	96.0	91.3

[a] $m_{VA\text{-}044\ initial}$ represents the sum of the initiator added $m_{VA\text{-}044\ added}$ + the amount of initiator remaining from the previous block. [b] represents the sum of the volume of the solvent added + volume of the monomer added + V_{total} previous block; [c] theoretical estimation of the fraction of living chains per block (e.g. extendable chains having the Z group); [d] theoretical estimation of the cumulated fraction of living chains

Table S14. Experimental conditions for the preparation of the diblock copolymer $PNAM_{150}$-*b*-$PDMA_{150}$ (Scheme 4, multiblock **n**) in H_2O/dioxane at 100˚C with VA-044 as initiator (3 min per block, in the presence of air, and without degassing).

Cycles	1	2
Monomer	NAM	DMA
$DP_{targeted}$	150	150
$m_{monomer\ added}$ (mg)	500	527
$m_{CTA\ added}$ (mg)	5.6	
$m_{VA\text{-}044\ added}$ (mg)	0.231	0.491
$m_{VA\text{-}044\ initial}$ [a] (mg)	0.231	0.583
V_{H2O} (mL)	0.510	0.781
$V_{dioxane\ added}$ (mL)	0.057	0
% H_2O	89.9	95.8
V_{total} [b] (mL)	1.012	2.341
$[VA\text{-}044]_0$ ($mol.L^{-1}$)	$7.1\ 10^{-4}$	$7.7\ 10^{-4}$
$[M]_0$ ($mol.L^{-1}$)	3.50	2.27
$[CTA]_0/[VA\text{-}044]_0$	33	13
L[c] (%)	98.2	94.8
Cumulative L[d] (%)	98.2	93.1

[a] $m_{VA\text{-}044\ initial}$ represents the sum of the initiator added $m_{VA\text{-}044\ added}$ + the amount of initiator remaining from the previous block. [b] represents the sum of the volume of the solvent added + volume of the monomer added + V_{total} previous block; [c] theoretical estimation of the fraction of living chains per block (e.g. extendable chains having the Z group); [d] theoretical estimation of the cumulated fraction of living chains

Table S15. Experimental conditions for the preparation of the diblock copolymer $PNAM_{200}$-*b*-$PDMA_{200}$ (Scheme 4, multiblock **o**) in H_2O/dioxane at 100˚C with VA-044 as initiator (3 min per block, in the presence of air, and without degassing).

Cycles	1	2
Monomer	NAM	DMA
$DP_{targeted}$	200	200
$m_{monomer\ added}$ (mg)	500	702
$m_{CTA\ added}$ (mg)	4.2	
$m_{VA\text{-}044\ added}$ (mg)	0.229	0.636
$m_{VA\text{-}044\ initial}$ [a] (mg)	0.229	0.728
V_{H2O} (mL)	0.510	1.041
$V_{dioxane\ added}$ (mL)	0.057	0
% H_2O	89.9	96.5
V_{total} [b] (mL)	1.012	2.783
$[VA\text{-}044]_0$ ($mol.L^{-1}$)	7.0 10^{-4}	8.1 10^{-4}
$[M]_0$ ($mol.L^{-1}$)	3.50	2.55
$[CTA]_0/[VA\text{-}044]_0$	25	8
L[c] (%)	96.2	88.7
Cumulative L[d] (%)	96.2	85.3

[a] $m_{VA\text{-}044\ initial}$ represents the sum of the initiator added $m_{VA\text{-}044\ added}$ + the amount of initiator remaining from the previous block. [b] represents the sum of the volume of the solvent added + volume of the monomer added + V_{total} previous block; [c] theoretical estimation of the fraction of living chains per block (e.g. extendable chains having the Z group); [d] theoretical estimation of the cumulated fraction of living chains