Electronic Supplementary Information for

Ultrafast RAFT Polymerization:

Multiblock Copolymers within Minutes

Guillaume Gody[‡],^{1,*} Raphael Barbey[‡], Maarten Danial[‡],² and Sébastien Perrier^{1,3,*}

Key Centre for Polymers & Colloids, School of Chemistry, The University of Sydney, NSW 2006, Sydney, Australia.

[‡]These authors contributed equally.

Present addresses:

¹ Department of Chemistry, The University of Warwick, CV4 7AL, UK.

² CSIRO Manufacturing Flagship, Bayview Ave., Clayton VIC 3168, Australia.

³ Faculty of Pharmacy and Pharmaceutical Sciences, Monash University, VIC 3052, Australia

Correspondence to: Email <u>g.gody@warwick.ac.uk</u> (G.G.); Email <u>s.perrier@warwick.ac.uk</u> (S.P.); Fax +44 2476 524112; Tel +44 2476 528085.

Figure S1:	Fraction of azoinitiator VA-044 consumed during the synthesis of the first two blocks PNAM ₂₀ - <i>b</i> -PNAM ₂₀ at 100°C4
Equation S1:	Method to determine the decomposition rate constant <i>k</i> _d
Figure S2:	Comparison of the temperature profiles obtained in conventional radical polymerization and RAFT polymerization
Figure S3:	¹ H NMR spectrum of the RAFT homopolymerization of NAM (DP = 20) at 100°C
Figure S4:	Comparison of the temperature profiles obtained in RAFT polymerization (with or without azoinitiator) and in conventional radical polymerization 8
Figure S5:	Temperature profile / monomer conversion / fraction of VA-044 consumed in NAM RAFT homopolymerization (DP = 20) at 100°C
Figure S6:	SEC chromatogram of the PNAM ₂₀ synthesized at 100°C10
Figure S7:	Comparison of SEC chromatograms of PNAM ₂₀ synthesized at 70°C (2 hours) or 100°C (3 min)
Figure S8:	ESI-ToF spectrum of the PNAM ₁₀ synthesized at 100°C 12
Figure S9:	Monomer conversion / SEC chromatograms / molar mass and <i>Đ</i> data obtained for the synthesis of the multiblock b
Figure S10:	Monomer conversion / SEC chromatograms / molar mass and <i>Đ</i> data obtained for the synthesis of the multiblock c
Figure S11:	Monomer conversion / SEC chromatograms / molar mass and <i>Đ</i> data obtained for the synthesis of the multiblock d 15
Figure S12:	Monomer conversion / SEC chromatograms / molar mass and <i>Đ</i> data obtained for the synthesis of the multiblock e
Figure S13:	SEC chromatograms / molar mass and \mathcal{D} data obtained for the synthesis of the homopolymer f
Figure S14:	SEC chromatograms / molar mass and \mathcal{D} data obtained for the synthesis of the homopolymer g
Figure S15:	Influence of a thermoresponsive block PDEA ₂₀ on the molar mass control for two pentablock copolymers. SEC chromatograms comparison 19
Figure S16:	SEC chromatograms / molar mass and <i>D</i> data obtained for the synthesis of the multiblock i
Figure S17:	SEC chromatograms / molar mass and <i>D</i> data obtained for the synthesis of the multiblock j
Figure S18:	SEC chromatograms / molar mass and \mathcal{P} data obtained for the synthesis of the multiblock k

Figure S19:	SEC chromatograms / molar mass and <i>Đ</i> data obtained for the synthesis of the multiblock 1
Figure S20:	SEC chromatograms / molar mass and <i>Đ</i> data obtained for the synthesis of the multiblock m
Figure S21:	SEC chromatograms / molar mass and <i>Đ</i> data obtained for the synthesis of the multiblock n
Figure S22:	SEC chromatograms / molar mass and <i>Đ</i> data obtained for the synthesis of the multiblock o
Table S1:	Experimental conditions for the preparation of the multiblock a 27
Table S2:	Experimental conditions for the preparation of the multiblock b28
Table S3:	Experimental conditions for the preparation of the multiblock c
Table S4:	Experimental conditions for the preparation of the multiblock d30
Table S5:	Experimental conditions for the preparation of the multiblock e
Table S6:	Experimental conditions for the preparation of the multiblock f
Table S7:	Experimental conditions for the preparation of the multiblock g33
Table S8:	Experimental conditions for the preparation of the multiblock h34
Table S9:	Experimental conditions for the preparation of the multiblock i
Table S10:	Experimental conditions for the preparation of the multiblock j
Table S11:	Experimental conditions for the preparation of the multiblock k37
Table S12:	Experimental conditions for the preparation of the multiblock 1
Table S13:	Experimental conditions for the preparation of the multiblock m
Table S14:	Experimental conditions for the preparation of the multiblock n40
Table S15:	Experimental conditions for the preparation of the multiblock o



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 PNAM₂₀-*b*-PNAM₂₀ via RAFT polymerization in the presence of air and without degassing (oil bath thermostated at 100°C).

Method to determine the decomposition rate constant $k_{\rm d}$

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).

 $k_{\rm d}$ values for VA-044 are determined by using Equation S1 based on the temperature profile recorded (Figure S5):

$$A = \frac{k_{d(317K)}}{e^{\frac{-E_{A}}{RT_{(317K)}}}} = \frac{k_{d(x K)}}{e^{\frac{-E_{A}}{RT_{(x K)}}}}$$
(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 PNAM₂₀.

T (K) kcl/\(\lambda \), Tune (s) V(\\(\lambda \), V(\(\lambda \), V(\									0.000	0.00 .
301.800 2.44E-68 6 1.000 0.000 301.800 2.34E-68 1.000 0.000 318.600 2.34E-66 1.000 0.000 318.600 2.34E-66 1.000 0.000 318.600 2.34E-66 1.000 0.000 317.00 7.32E-66 1.6 1.000 0.000 331.700 7.32E-66 1.6 1.000 0.000 331.700 7.32E-64 1.000 0.000 343.400 4.48E-04 2.0 0.999 0.001 346.800 6.66E-04 2.6 0.996 0.002 348.800 6.66E-04 2.6 0.996 0.001 352.600 1.36E-04 2.6 0.999 0.010 354.800 6.66E-04 2.0 0.998 0.022 355.600 1.46E-03 3.0 0.997 0.010 356.600 1.46E-03 3.0 0.980 0.022 355.600 1.46E-03 3.0 0.98	т (К)	kd(VA-044)	Time (s)	[VA-044]t	[VA-044]consumed	370.100	7.47E-03	90	0.686	0.314
301.500 2.34E-68 8 1.000 0.000 370.500 7.18E-43 94. 0.666 0.334 312.200 1.002-65 10 1.000 0.000 370.500 7.18E-43 96. 0.656 0.334 313.600 2.38E-68 12 1.000 0.000 369.700 7.18E-43 96. 0.657 0.333 32.700 7.32E-68 16 10.00 0.000 369.400 6.42E-43 102 0.631 0.369 337.000 2.24E-64 22 0.999 0.001 369.400 6.42E-43 102 0.615 0.335 344.00 4.48E-04 24 0.998 0.002 369.500 6.48E-03 110 0.599 0.401 345.500 1.48E-03 23 0.999 0.007 369.500 6.48E-03 110 0.599 0.401 356.500 1.48E-03 23 0.937 0.013 368.500 6.67E-03 118 0.586 0.432	301.800	2.44E-06	6	1.000	0.000	370.300	7.47E-03	92	0.675	0.325
312.200 1.02E-06 10 1.000 0.000 369.700 7.18E-03 96. 0.656 0.344 318.600 2.38E-06 1.4 1.000 0.000 369.300 6.42E-03 100 0.631 0.353 327.700 7.32E-05 1.6 1.000 0.000 369.400 6.42E-03 100 0.631 0.369 337.000 1.16E-04 18 0.999 0.001 369.400 6.42E-03 100 0.615 0.385 338.000 2.276E-04 20 0.998 0.002 369.500 6.48E-03 106 0.615 0.385 344.000 4.48E-04 24 0.998 0.002 369.500 6.48E-03 110 0.599 0.401 356.600 1.48E-03 34 0.997 0.010 369.600 6.48E-03 116 0.576 0.424 355.600 1.48E-03 34 0.987 0.016 368.500 6.67E-03 120 0.551 0.432 3	301.500	2.34E-06	8	1.000	0.000	370.500	7.13E-03	94	0.666	0.334
318.600 2.38E-05 12 1.000 0.000 323.400 4.32E-05 1.4 1.000 0.000 337.400 7.32E-05 1.6 1.000 0.000 337.400 2.28E-04 20 0.999 0.001 369.400 6.42E-03 102 0.631 0.369 337.400 2.74E-04 22 0.998 0.002 344.800 4.48E-04 2.6 0.996 0.002 346.900 6.58E-04 2.6 0.996 0.002 348.00 8.0E-04 2.6 0.996 0.002 348.00 8.0E-04 2.6 0.996 0.002 348.00 0.98E-04 3.0 0.993 0.007 356.400 1.28E-03 3.2 0.990 0.010 355.800 9.98E-04 3.0 0.987 0.013 365.400 1.78E-03 3.6 0.984 0.016 355.900 4.986-3 0.995 0.042 <t< th=""><th>312.200</th><th>1.02E-05</th><th>10</th><th>1.000</th><th>0.000</th><th>369.700</th><th>7.13E-03</th><th>96</th><th>0.656</th><th>0.344</th></t<>	312.200	1.02E-05	10	1.000	0.000	369.700	7.13E-03	96	0.656	0.344
123.400 4.32E-05 14 1.000 0.000 327.700 7.32E-05 16 1.000 0.000 337.700 7.4E-04 22 0.999 0.001 369.400 6.42E-03 100 0.633 0.337 34.400 4.48E-04 24 0.998 0.002 369.500 6.48E-03 110 0.599 0.401 348.800 6.68E-04 26 0.9995 0.005 369.600 6.48E-03 111 0.584 0.416 352.600 1.4E-03 34 0.987 0.013 368.900 6.67E-03 113 0.585 0.424 353.100 2.44E-03 32 0.999 0.021 368.700 6.67E-03 122 0.531 0.447 353.100 2.44E-03 32 0.99	318.600	2.36E-05	12	1.000	0.000	369.500	7.13E-03	98	0.647	0.353
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 0.001 337.400 2.29E-04 20 0.999 0.001 346.900 6.58E-04 22 0.998 0.002 346.900 6.58E-04 26 0.999 0.001 350.800 998E-04 30 0.993 0.007 369.500 6.48E-03 112 0.591 0.409 352.800 998E-04 30 0.993 0.007 369.500 6.48E-03 116 0.576 0.424 352.800 998E-04 36 0.984 0.016 356.400 1.28E-03 38 0.980 0.020 356.400 1.28E-03 38 0.980 0.021 366.700 6.7E-03 124 0.546 0.432 366.800 5.88E-03 6.87E-03 132 0.513 <th< th=""><th>323.400</th><th>4.32E-05</th><th>14</th><th>1.000</th><th>0.000</th><th>369.400</th><th>6.42E-03</th><th>100</th><th>0.639</th><th>0.361</th></th<>	323.400	4.32E-05	14	1.000	0.000	369.400	6.42E-03	100	0.639	0.361
331.700 1:18E-44 18 0.999 0.001 337.400 2:28E-04 20 0.999 0.001 339.000 2:74E-04 22 0.998 0.002 343.400 4:48E-04 22 0.998 0.002 346.500 6:56E-04 22 0.998 0.002 346.500 6:56E-04 28 0.995 0.005 352.600 9:8E-04 30 0.993 0.007 354.400 1:46E-03 34 0.995 0.005 356.400 1:46E-03 34 0.996 0.004 356.400 1:46E-03 34 0.997 0.013 366.400 6:47E-03 118 0.568 0.432 356.400 1:46E-03 34 0.987 0.020 365.400 6:47E-03 124 0.561 0.432 365.400 4:567-03 122 0.553 0.445 365.400 4:67E-03 124 0.564 0.4454	327.700	7.32E-05	16	1.000	0.000	369.400	6.42E-03	102	0.631	0.369
337.000 2.28E-04 20 0.999 0.001 339.000 2.78E-04 22 0.998 0.002 343.000 4.48E-04 22 0.998 0.002 346.000 6.56E-04 26 0.996 0.002 348.300 6.56E-04 26 0.996 0.001 350.800 9.98E-04 30 0.993 0.007 354.500 1.46E-03 31 0.556 0.424 355.400 1.46E-03 32 0.990 0.010 365.400 1.78E-03 36 0.984 0.016 355.700 2.48E-03 318 0.568 0.432 355.700 2.48E-03 44 0.963 0.037 366.700 6.67E-03 122 0.553 0.441 365.700 6.67E-03 128 0.531 0.461 365.700 6.67E-03 130 0.524 0.476 364.200 3.88 0.936 0.064 366.600 <	331.700	1.18E-04	18	0.999	0.001	369.400	6.42E-03	104	0.623	0.377
333.000 2.74E-04 22 0.998 0.002 343.400 4.48E-04 24 0.998 0.002 346.900 6.56E-04 28 0.995 0.0004 350.800 9.95E-04 28 0.995 0.0007 356.400 1.20E-03 32 0.993 0.007 356.400 1.20E-03 34 0.987 0.010 356.400 1.78E-03 34 0.987 0.011 366.500 6.47E-03 118 0.568 0.424 356.400 1.78E-03 36 0.984 0.016 368.700 6.67E-03 122 0.553 0.447 361.200 2.84E-03 42 0.969 0.031 362.600 3.32E-03 44 0.663 0.037 364.500 6.47E-03 124 0.544 0.461 365.600 5.40-35 0.0454 368.600 5.96E-03 132 0.511 0.482 365.600 5.86E-03	337.400	2.29E-04	20	0.999	0.001	369.500	6.48E-03	106	0.615	0.385
333.400 4.48E-04 24 0.998 0.002 346.900 6.56E-04 25 0.996 0.004 386.800 8.08E-04 28 0.995 0.005 382.600 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 0.010 358.100 2.46E-03 40 0.975 0.025 366.700 6.67E-03 122 0.551 0.447 358.100 2.46E-03 40 0.975 0.025 366.700 6.67E-03 124 0.546 0.442 362.600 3.32E-03 44 0.963 0.037 364.200 3.86E-03 44 0.955 0.045 366.800 6.87E-03 128 0.524 0.476 367.000 6.87E-03 138 0.524 0.478 367.000 6.88E-03 52 0.925 0.067	339.000	2.74E-04	22	0.998	0.002	369.500	6.48E-03	108	0.607	0.393
336,900 6.58E-04 26 0.995 0.004 348,800 8.05E-04 28 0.995 0.005 350,800 9.95E-04 28 0.995 0.007 352,600 1.02E-03 32 0.990 0.010 356,400 1.48E-03 34 0.987 0.011 356,400 1.72E-03 38 0.987 0.012 356,400 1.72E-03 38 0.987 0.012 356,400 1.22E-03 38 0.987 0.020 366,200 2.98E-03 42 0.969 0.031 366,200 3.82E-03 44 0.965 0.045 366,200 5.87E-03 122 0.518 0.462 365,500 5.48E-03 52 0.925 0.075 368.700 6.67E-03 130 0.524 0.476 365,500 5.48E-03 52 0.925 0.075 368.600 5.98E-03 136 0.505 0.4482 366,000	343.400	4.48E-04	24	0.998	0.002	369.600	6.48E-03	110	0.599	0.401
338.800 8.06:04 28 0.995 0.005 336.800 9.95:04 30 0.993 0.007 352.600 1.20E-03 32 0.990 0.010 354.500 1.46E-03 34 0.987 0.013 354.600 1.78E-03 34 0.987 0.013 358.100 2.12E-03 38 0.980 0.020 355.700 2.49E-03 40 0.975 0.025 366.800 6.67E-03 124 0.566 0.447 352.600 3.32E-03 44 0.963 0.037 364.200 3.89E-03 44 0.963 0.037 365.000 5.98E-03 48 0.947 0.053 366.700 5.41E-03 52 0.925 0.045 368.500 5.89E-03 48 0.947 0.053 371.400 7.76E-03 52 0.925 0.075 371.400 7.86E-03 60 0.86E-03 144 0.	346.900	6.56E-04	26	0.996	0.004	369.600	6.48E-03	112	0.591	0.409
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 0.987 0.013 356.400 1.78E-03 36 0.987 0.013 356.400 1.78E-03 36 0.984 0.016 358.700 6.47E-03 122 0.553 0.447 358.700 2.49E-03 42 0.969 0.031 368.700 6.67E-03 122 0.534 0.451 364.200 3.89E-03 44 0.963 0.037 368.700 6.67E-03 132 0.518 0.4482 365.900 4.99E-03 48 0.947 0.053 368.600 6.67E-03 132 0.518 0.4482 365.500 5.49E-03 0.936 0.0644 368.600 5.95E-03 144 0.505 0.448 372.000 8.21E-03 54	348.800	8.05E-04	28	0.995	0.005	369.700	6.48E-03	114	0.584	0.416
332.600 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 0.020 358.100 2.48E-03 40 0.975 0.025 362.600 3.32E-03 42 0.969 0.031 362.600 3.32E-03 44 0.963 0.037 365.900 4.59E-03 42 0.551 0.045 365.900 4.59E-03 44 0.963 0.037 365.900 5.49E-03 44 0.963 0.037 365.900 5.49E-03 1.30 0.524 0.476 365.900 5.49E-03 1.32 0.518 0.482 366.800 5.96E-03 132 0.518 0.482 366.800 5.96E-03 133 0.495 0.485 366.800 5.96E-03 144 0.487 0.513 <th>350.800</th> <th>9.95E-04</th> <th>30</th> <th>0.993</th> <th>0.007</th> <th>369.800</th> <th>6.67E-03</th> <th>116</th> <th>0.576</th> <th>0.424</th>	350.800	9.95E-04	30	0.993	0.007	369.800	6.67E-03	116	0.576	0.424
354.500 1.46E-03 34 0.987 0.013 368.900 6.67E-03 120 0.561 0.439 356.400 1.78E-03 36 0.984 0.016 368.900 6.67E-03 122 0.553 0.447 359.700 2.49E-03 40 0.975 0.025 368.700 6.67E-03 122 0.533 0.447 362.600 3.32E-03 42 0.969 0.031 368.700 6.67E-03 126 0.531 0.459 364.200 3.88E-03 44 0.963 0.037 368.700 6.67E-03 120 0.518 0.449 365.900 4.59E-03 48 0.947 0.053 368.700 6.67E-03 130 0.524 0.476 366.800 5.89E-03 134 0.511 0.489 367.600 5.89E-03 136 0.505 0.445 372.000 8.48E-03 56 0.899 0.101 368.600 5.98E-03 140 0.499 0.501	352.600	1.20E-03	32	0.990	0.010	368.900	6.67E-03	118	0.568	0.432
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 42 0.969 0.031 366.700 6.67E-03 124 0.546 0.454 361.200 2.89E-03 42 0.969 0.031 368.700 6.67E-03 128 0.531 0.461 362.200 3.39E-03 44 0.963 0.037 368.700 6.67E-03 130 0.524 0.476 365.900 4.59E-03 48 0.947 0.053 368.600 6.67E-03 130 0.511 0.489 370.100 6.88E-03 52 0.925 0.075 368.600 5.95E-03 138 0.499 0.501 371.400 7.76E-03 56 0.899 0.101 368.600 5.95E-03 142 0.487 0.513 372.200 8.45E-03 64 0.840 0.160 368.600 5.95E-03 146 0.475	354.500	1.46E-03	34	0.987	0.013	368.900	6.67E-03	120	0.561	0.439
358.100 2.12E-03 38 0.980 0.020 358.100 2.42E-03 40 0.975 0.025 361.200 2.89E-03 42 0.969 0.031 362.600 3.32E-03 42 0.969 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 52 0.925 0.045 368.500 5.89E-03 52 0.925 0.075 368.600 5.98E-03 132 0.518 0.482 368.500 5.89E-03 52 0.925 0.075 371.400 7.76E-03 56 0.899 0.101 372.300 8.45E-03 60 0.869 0.131 372.400 8.5E-03 64 0.840 0.160 372.200 8.45E-03 66 0.821 0.88 372.200 8.45E-03 63 0.812 0.88 <t< th=""><th>356.400</th><th>1.78E-03</th><th>36</th><th>0.984</th><th>0.016</th><th>368.900</th><th>6.67E-03</th><th>122</th><th>0.553</th><th>0.447</th></t<>	356.400	1.78E-03	36	0.984	0.016	368.900	6.67E-03	122	0.553	0.447
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 0.053 365.900 4.59E-03 48 0.947 0.053 368.700 6.67E-03 134 0.511 0.489 367.600 5.41E-03 50 0.935 0.064 368.600 5.9EE-03 136 0.505 0.495 370.100 6.86E-03 56 0.899 0.101 368.600 5.9EE-03 140 0.493 0.507 371.400 7.76E-03 56 0.899 0.131 368.600 5.9EE-03 144 0.481 0.513 372.300 8.45E-03 66 0.826 0.174 368.600 5.9EE-03 144 0.443 0.552 372.400 8.52E-03 66<	358.100	2.12E-03	38	0.980	0.020	368.700	6.67E-03	124	0.546	0.454
361.200 2.88E-03 42 0.969 0.031 361.200 3.28E-03 44 0.963 0.037 364.200 3.88E-03 46 0.955 0.045 365.900 4.59E-03 48 0.947 0.053 367.600 5.41E-03 50 0.936 0.064 370.100 6.86E-03 52 0.925 0.075 371.400 7.76E-03 54 0.913 0.087 371.400 7.76E-03 56 0.899 0.101 372.300 8.45E-03 60 0.869 0.131 372.300 8.45E-03 62 0.855 0.145 372.300 8.45E-03 66 0.826 0.174 372.300 8.45E-03 66 0.826 0.174 372.300 8.45E-03 68 0.812 0.188 372.300 8.45E-03 68 0.812 0.188 372.300 8.45E-03 68 0.124 368.600	359.700	2.49E-03	40	0.975	0.025	368.700	6.67E-03	126	0.539	0.461
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 0.087 372.000 8.21E-03 56 0.899 0.101 372.300 8.45E-03 60 0.8669 0.131 372.300 8.45E-03 66 0.826 0.174 372.300 8.45E-03 68 0.812 0.188 372.300 8.45E-03 74 0.773 0.227 372.000 8.21E-03 72 0.786 0.214	361.200	2.89E-03	42	0.969	0.031	368.700	6.67E-03	128	0.531	0.469
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 5.88E-03 52 0.925 0.075 370.100 6.86E-03 54 0.913 0.087 372.300 8.46E-03 56 0.889 0.101 372.300 8.46E-03 62 0.885 0.145 372.300 8.46E-03 62 0.885 0.145 372.300 8.46E-03 66 0.826 0.174 372.300 8.46E-03 66 0.826 0.174 372.300 8.46E-03 66 0.826 0.174 372.300 8.46E-03 68 0.812 0.188 372.300 8.45E-03 66 0.826 0.174 372.300 8.45E-03 72 0.786 0.214 372.300 8.45E-03 74 0.773 0.227	362.600	3.32E-03	44	0.963	0.037	368.700	6.67E-03	130	0.524	0.476
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 0.131 372.400 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 0.188 372.000 8.21E-03 72 0.786 0.214 372.000 8.21E-03 72 0.786 0.214	364.200	3.89E-03	46	0.955	0.045	368.600	6.67E-03	132	0.518	0.482
367.6005.41E-03500.9360.064368.6005.95E-031360.5050.495368.5005.89E-03520.9250.075368.6005.95E-031400.4930.507371.4007.76E-03560.8990.101368.6005.95E-031400.4930.507372.0008.21E-03580.8840.116368.6005.95E-031420.4870.513372.3008.46E-03600.8690.131368.6005.95E-031440.4810.519372.3008.60E-03620.8550.145368.6005.95E-031440.4750.525372.3008.45E-03660.8260.174368.6005.95E-031500.4640.536372.3008.45E-03680.8120.188368.6005.95E-031520.4590.541372.2008.37E-03700.7990.201368.6005.95E-031560.4480.552371.0007.98E-03740.7730.227368.6005.95E-031560.4430.557371.0007.47E-03800.7390.261368.6005.95E-031640.4270.573370.6007.47E-03840.7170.283368.6005.95E-031660.4220.578370.6007.47E-03860.7060.294368.6005.95E-031660.4220.578370.0007.47E-03 <th>365.900</th> <th>4.59E-03</th> <th>48</th> <th>0.947</th> <th>0.053</th> <th>368.600</th> <th>6.67E-03</th> <th>134</th> <th>0.511</th> <th>0.489</th>	365.900	4.59E-03	48	0.947	0.053	368.600	6.67E-03	134	0.511	0.489
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 0.116 372.000 8.45E-03 60 0.869 0.131 372.000 8.60E-03 62 0.855 0.145 372.300 8.60E-03 66 0.869 0.131 372.400 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 0.201 372.200 8.21E-03 72 0.786 0.214 368.600 5.95E-03 156 0.448 0.557 371.700 7.76E-03 76 0.761 0.239 368.600 5.95E-03 160 0.437 0.563	367.600	5.41E-03	50	0.936	0.064	368.600	5.95E-03	136	0.505	0.495
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 0.131 372.400 8.52E-03 62 0.855 0.145 372.300 8.45E-03 66 0.826 0.174 372.300 8.45E-03 68 0.812 0.188 372.000 8.37E-03 70 0.799 0.201 372.000 8.21E-03 72 0.773 0.227 368.600 5.95E-03 158 0.443 0.557 371.000 7.47E-03 76 0.713 0.227 368.600 5.95E-03 160 0.437 0.563	368.500	5.89E-03	52	0.925	0.075	368.600	5.95E-03	138	0.499	0.501
371.4007.76E-03560.8990.101372.0008.21E-03580.8840.116372.3008.45E-03600.8690.131372.4008.60E-03620.8550.145372.3008.60E-03620.8400.160372.4008.52E-03640.8400.160372.3008.45E-03660.8260.174372.3008.45E-03660.8260.174372.0008.37E-03700.7990.201372.0008.37E-03700.7990.201372.0008.21E-03720.7860.214371.4007.76E-03760.7610.239371.4007.6E-03780.7500.250371.6007.47E-03820.7280.272371.6007.47E-03840.7170.283370.6007.47E-03880.6960.304370.0007.47E-03880.6960.304370.0007.47E-03880.6960.314370.1007.47E-03880.6960.304370.1007.47E-03880.6960.314	370.100	6.86E-03	54	0.913	0.087	368.600	5.95E-03	140	0.493	0.507
372.0008.21E-03580.8840.116372.3008.45E-03600.8690.131372.5008.60E-03620.8550.145372.4008.52E-03640.8400.160372.3008.45E-03660.8260.174372.3008.45E-03660.8260.174372.2008.37E-03700.7990.201372.0008.21E-03700.7990.201372.0008.21E-03720.7860.214372.0008.21E-03740.7730.227371.0007.47E-03760.7610.239371.0007.47E-03820.7280.272371.6007.47E-03820.7280.272370.0007.47E-03860.7060.294370.2007.47E-03880.6960.304370.2007.47E-03880.6960.304370.1007.47E-03890.6860.314	371.400	7.76E-03	56	0.899	0.101	368.600	5.95E-03	142	0.487	0.513
372.300 8.45E-03 60 0.869 0.131 372.300 8.45E-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 66 0.826 0.174 372.300 8.45E-03 68 0.812 0.188 372.300 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 0.214 368.600 5.95E-03 158 0.443 0.557 371.000 7.47E-03 76 0.761 0.239 371.000 7.47E-03 80 0.739 0.211 370.600 7.47E-03 82 0.728 0.272 371.600 7.47E-03 84 0.717 0.283 370.600 7.47E-03 84 0.717 0.284	372.000	8.21E-03	58	0.884	0.116	368.600	5.95E-03	144	0.481	0.519
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 66 0.826 0.174 372.300 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 0.201 368.600 5.95E-03 152 0.453 0.541 372.200 8.27E-03 72 0.786 0.214 376.00 7.78E-03 74 0.773 0.227 371.00 7.6E-03 76 0.761 0.239 371.000 7.47E-03 80 0.739 0.261 371.600 7.47E-03 82 0.728 0.272 371.600 7.47E-03 82 0.728 0.272 371.600 7.47E-03 84 0.717 0.283 <t< th=""><th>372.300</th><th>8.45E-03</th><th>60</th><th>0.869</th><th>0.131</th><th>368.600</th><th>5.95E-03</th><th>146</th><th>0.475</th><th>0.525</th></t<>	372.300	8.45E-03	60	0.869	0.131	368.600	5.95E-03	146	0.475	0.525
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 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 0.214 372.000 8.21E-03 72 0.786 0.214 371.700 7.98E-03 74 0.773 0.227 368.600 5.95E-03 160 0.432 0.563 371.000 7.76E-03 76 0.761 0.239 368.600 5.95E-03 160 0.432 0.563 371.000 7.47E-03 80 0.739 0.261 368.600 5.95E-03 164 0.427 0.573 371.600 7.47E-03 82 0.728 0.272 368.600 5.95E-03 166 0.422 0.578 370.600 7.47E-03 <th>372.500</th> <th>8.60E-03</th> <th>62</th> <th>0.855</th> <th>0.145</th> <th>368.600</th> <th>5.95E-03</th> <th>148</th> <th>0.470</th> <th>0.530</th>	372.500	8.60E-03	62	0.855	0.145	368.600	5.95E-03	148	0.470	0.530
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 0.201 372.300 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 0.214 368.600 5.95E-03 155 0.448 0.557 371.700 7.89E-03 76 0.761 0.239 368.600 5.95E-03 160 0.437 0.563 371.000 7.47E-03 80 0.750 0.250 368.600 5.95E-03 164 0.427 0.573 371.600 7.47E-03 80 0.739 0.261 368.600 5.95E-03 166 0.422 0.578 371.600 7.47E-03 84 0.717 0.283 368.600 5.95E-03 166 0.417 0.583 370.600 7.47E-03 84<	372.400	8.52E-03	64	0.840	0.160	368.600	5.95E-03	150	0.464	0.536
372.300 8.45E-03 68 0.812 0.188 372.200 8.37E-03 70 0.799 0.201 372.000 8.37E-03 70 0.799 0.201 372.000 8.21E-03 72 0.786 0.214 371.000 7.98E-03 74 0.773 0.227 371.400 7.76E-03 76 0.761 0.239 371.000 7.47E-03 80 0.739 0.261 371.600 7.47E-03 82 0.728 0.272 368.600 5.95E-03 164 0.427 0.573 371.600 7.47E-03 84 0.717 0.283 370.600 7.47E-03 84 0.717 0.283 370.200 7.47E-03 88 0.696 0.304 370.200 7.47E-03 88 0.696 0.304 370.100 7.47E-03 88 0.696 0.304 368.600 5.95E-03 174 0.402 0.598	372.300	8.45E-03	66	0.826	0.174	368.600	5.95E-03	152	0.459	0.541
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 0.227 371.700 7.98E-03 74 0.773 0.227 371.700 7.76E-03 76 0.761 0.239 371.200 7.47E-03 78 0.750 0.250 371.000 7.47E-03 80 0.739 0.261 371.600 7.47E-03 80 0.739 0.261 371.600 7.47E-03 82 0.728 0.272 371.600 7.47E-03 84 0.717 0.283 370.500 7.47E-03 86 0.706 0.294 368.600 5.95E-03 166 0.412 0.583 370.300 7.47E-03 88 0.696 0.304 368.600 5.95E-03 170 0.412 0.588 370.300 7.47E-03 88 0.696 0.304 368.600	372.300	8.45E-03	68	0.812	0.188	368.600	5.95E-03	154	0.453	0.547
372.000 8.21E-03 72 0.786 0.214 371.700 7.98E-03 74 0.773 0.227 371.700 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 0.272 371.600 7.47E-03 84 0.717 0.283 370.600 7.47E-03 86 0.706 0.294 370.300 7.47E-03 88 0.696 0.304 370.200 7.47E-03 88 0.696 0.304 370.200 7.47E-03 88 0.696 0.304 370.200 7.47E-03 88 0.696 0.304 370.000 7.47E-03 88 0.696 0.304 368.600 5.95E-03 170 0.412 0.588	372.200	8.37E-03	70	0.799	0.201	368.600	5.95E-03	156	0.448	0.552
371.700 7.98E-03 74 0.773 0.227 368.600 5.95E-03 160 0.437 0.563 371.400 7.76E-03 76 0.761 0.239 368.600 5.95E-03 162 0.437 0.563 371.200 7.62E-03 78 0.750 0.250 368.600 5.95E-03 164 0.427 0.573 371.000 7.47E-03 80 0.739 0.261 368.600 5.95E-03 166 0.422 0.578 371.600 7.47E-03 82 0.728 0.272 368.600 5.95E-03 168 0.417 0.583 370.600 7.47E-03 84 0.717 0.283 368.600 5.95E-03 170 0.412 0.588 370.200 7.47E-03 86 0.706 0.294 368.600 5.95E-03 172 0.407 0.593 370.000 7.47E-03 88 0.696 0.304 368.600 5.95E-03 174 0.402 0.598	372.000	8.21E-03	72	0.786	0.214	368.600	5.95E-03	158	0.443	0.557
371.400 7.76E-03 76 0.761 0.239 368.600 5.95E-03 162 0.432 0.568 371.200 7.62E-03 78 0.750 0.250 368.600 5.95E-03 164 0.427 0.573 371.000 7.47E-03 80 0.739 0.261 368.600 5.95E-03 166 0.422 0.578 371.600 7.47E-03 82 0.728 0.272 368.600 5.95E-03 166 0.417 0.583 370.600 7.47E-03 84 0.717 0.283 368.600 5.95E-03 170 0.412 0.588 370.500 7.47E-03 86 0.706 0.294 368.600 5.95E-03 172 0.407 0.593 370.200 7.47E-03 88 0.696 0.304 368.600 5.95E-03 174 0.402 0.598 370.100 7.47E-03 90 0.686 0.314 368.600 5.95E-03 176 0.398 0.602	371.700	7.98E-03	74	0.773	0.227	368.600	5.95E-03	160	0.437	0.563
371.200 7.62E-03 78 0.750 0.250 368.600 5.95E-03 164 0.427 0.573 371.000 7.47E-03 80 0.739 0.261 368.600 5.95E-03 166 0.422 0.578 371.600 7.47E-03 82 0.728 0.272 368.600 5.95E-03 166 0.422 0.578 370.600 7.47E-03 84 0.717 0.283 368.600 5.95E-03 168 0.417 0.583 370.200 7.47E-03 86 0.706 0.294 368.600 5.95E-03 170 0.412 0.588 370.200 7.47E-03 88 0.696 0.304 368.600 5.95E-03 174 0.402 0.598 370.100 7.47E-03 90 0.686 0.314 368.600 5.95E-03 176 0.398 0.602	371.400	7.76E-03	76	0.761	0.239	368.600	5.95E-03	162	0.432	0.568
371.000 7.47E-03 80 0.739 0.261 368.600 5.95E-03 166 0.422 0.578 371.600 7.47E-03 82 0.728 0.272 368.600 5.95E-03 168 0.417 0.583 370.600 7.47E-03 84 0.717 0.283 368.600 5.95E-03 170 0.412 0.588 370.300 7.47E-03 86 0.706 0.294 368.600 5.95E-03 172 0.407 0.593 370.200 7.47E-03 88 0.696 0.304 368.600 5.95E-03 174 0.402 0.598 370.100 7.47E-03 90 0.686 0.314 368.600 5.95E-03 176 0.398 0.602	371.200	7.62E-03	78	0.750	0.250	368.600	5.95E-03	164	0.427	0.573
371.600 7.47E-03 82 0.728 0.272 368.600 5.95E-03 168 0.417 0.583 370.600 7.47E-03 84 0.717 0.283 368.600 5.95E-03 170 0.412 0.588 370.300 7.47E-03 86 0.706 0.294 368.600 5.95E-03 172 0.407 0.593 370.200 7.47E-03 88 0.696 0.304 368.600 5.95E-03 174 0.402 0.598 370.100 7.47E-03 90 0.686 0.314 368.600 5.95E-03 176 0.398 0.602	371.000	7.47E-03	80	0.739	0.261	368.600	5.95E-03	166	0.422	0.578
370.600 7.47E-03 84 0.717 0.283 368.600 5.95E-03 170 0.412 0.588 370.300 7.47E-03 86 0.706 0.294 368.600 5.95E-03 172 0.407 0.593 370.200 7.47E-03 88 0.696 0.304 368.600 5.95E-03 174 0.402 0.598 370.100 7.47E-03 90 0.686 0.314 368.600 5.95E-03 176 0.398 0.602	371.600	7.47E-03	82	0.728	0.272	368.600	5.95E-03	168	0.417	0.583
370.300 7.47E-03 86 0.706 0.294 368.600 5.95E-03 172 0.407 0.593 370.200 7.47E-03 88 0.696 0.304 368.600 5.95E-03 174 0.402 0.598 370.100 7.47E-03 90 0.686 0.314 368.600 5.95E-03 176 0.398 0.602	370.600	7.47E-03	84	0.717	0.283	368.600	5.95E-03	170	0.412	0.588
370.200 7.47E-03 88 0.696 0.304 368.600 5.95E-03 174 0.402 0.598 370.100 7.47E-03 90 0.686 0.314 368.600 5.95E-03 176 0.398 0.602	370.300	7.47E-03	86	0.706	0.294	368.600	5.95E-03	172	0.407	0.593
370.100 7.47E-03 90 0.686 0.314 368.600 5.95E-03 176 0.398 0.602	370.200	7.47E-03	88	0.696	0.304	368.600	5.95E-03	174	0.402	0.598
	370.100	7.47E-03	90	0.686	0.314	368.600	5.95E-03	176	0.398	0.602



Figure S2. (a) Comparison of the ¹H NMR spectra (DMSO- d_6 , 300 MHz) of the RAFT agent PABTC after 0, 3, and 21 minutes in a mixture H₂O/dioxane (80/20, v/v). Peak integration shows no degradation of the CTA. b) ¹H NMR spectrum (DMSO- d_6 , 300 MHz) of the mixture of NAM and chain transfer agent (without azoinitiator) after 3 min in H₂O/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. ¹H NMR spectrum (D₂O, 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 H₂O/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-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 PNAM₂₀ (DP_{targeted} = 20, Table S2, cycle 1) synthesized by ultrafast RAFT polymerization in the same conditions (H₂O/dioxane : 80/20, ν/ν 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 PNAM₂₀ synthesized with VA-044 as azoinitiator, in H₂O/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/H₂O (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) ¹H NMR spectra (D₂O, 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 [PNAM₂₀]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 [PNAM₂₀]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) ¹H NMR spectra (D₂O, 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 [PNAM₅₀]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 [PNAM₅₀]₅. The black line represents the theoretical molar masses obtained by THF SEC. The empty squares represent the dispersity values as determined by THF SEC.



Figure S11. (a) ¹H NMR spectra (D₂O, 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 [PNAM₁₀₀]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 [PNAM₁₀₀]₄. The black line represents the theoretical molar masses obtained by THF SEC. The empty squares represent the dispersity values as determined by THF SEC.



Figure S12. (a) ¹H NMR spectra (D₂O, 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 [PNAM₂₀₀]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 [PNAM₂₀₀]₃. The black line represents the theoretical 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*-PDMA₂₀-*b*-PDEA₂₀-*b*-PHEAm₂₀-*b*-PNAM₂₀ and (b) $PNAM_{20}$ -*b*-PDMA₂₀-*b*-PDMA₂₀-*b*-PDEA₂₀ showing the impact of having the thermoresponsive block PDEA₂₀ 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) ¹H NMR spectra (D₂O, 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 PNAM₂₀-*b*-PDMA₂₀-*b*-PNAM₂₀-*b*-PHEAm₂₀-*b*-PDEA₂₀ (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.



Figure S17. (a) ¹H NMR spectra (D₂O, 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 PNAM₅₀-*b*-PDMA₅₀-*b*-PHEAm₅₀-*b*-PDEA₅₀ (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.



Figure S18. (a) ¹H NMR spectra (D₂O, 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 PNAM₂₀-*b*-PDMA₂₀-*b*-PHEAm₂₀ (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) ¹H 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 PNAM₂₀-*b*-PDMA₂₀-*b*-PDEA₂₀ (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.



Figure S20. (a) ¹H NMR spectra (D₂O, 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 PNAM₁₀₀-*b*-PDMA₁₀₀-*b*-PDEA₁₀₀ (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) ¹H 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 PNAM₁₅₀-*b*-PDMA₁₅₀ (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) ¹H NMR spectra (D₂O, 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 PNAM₂₀₀-*b*-PDMA₂₀₀ (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.

Cycles	1	2	3	4	5	6	7
Monomer	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	-	-	-	-	-	-
$m_{VA-044 added} (mg)$	0.611	0.458	0.705	0.916	1.145	1.409	1.666
m _{VA-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 ₂ O	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-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-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

Table S1. Experimental conditions for the preparation of the heptablock [PNAM₁₀]₇ (Scheme 3, multiblock **a**) in H₂O/dioxane at 100°C with VA-044 as initiator (3 min per block, in the presence of air, and without degassing).

Table S2. Experimental conditions for the preparation of the hexablock $[PNAM_{20}]_6$ (Scheme 3, multiblock **b**) in H₂O/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	-	-	-	-	-
$m_{VA-044 added} (mg)$	0.458	0.458	0.705	0.916	1.145	1.309
m _{vA-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 ₂ O	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-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-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

Table S3. Experimental conditions for the preparation of the pentablock [PNAM₅₀]₅ (Scheme 3, multiblock c) in H₂O/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-044 added} (mg)	0.229	0.366	0.555	0.733	0.916
m _{VA-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 ₂ O	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-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-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

Table S4. Experimental conditions for the preparation of the tetrablock $[PNAM_{100}]_4$ (Scheme 3, multiblock **d**) in H₂O/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	-	-	-
$m_{VA-044 added} (mg)$	0.183	0.395	0.458	0.611
m _{VA-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 ₂ O	94.9	97.7	98.4	98.7
V _{total} ^[b] (mL)	0.810	1.733	2.542	3.352
[VA-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-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

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-044 added} (mg)	0.183	0.278	0.398
m _{VA-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 ₂ O	94.9	97.5	98.3
V _{total} ^[b] (mL)	0.810	1.619	2.429
[VA-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-044] ₀	25	13	9
L ^[c] (%)	97.7	94.8	92.8
Cumulative L ^[d] (%)	97.7	92.5	85.8

Table S5. Experimental conditions for the preparation of the triblock [PNAM₂₀₀]₃ (Scheme 3, multiblock e) in H₂O/dioxane at 100°C with VA-044 as initiator (3 min per block, in the presence of air, and without degassing).

Table S6. Experimental conditions for the preparation of $PNAM_{400}$ (Scheme 3, multiblock **f**) in H₂O/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-044 added} (mg)	0.191
V _{H2O added} (mL)	0.671
V _{dioxane added} (mL)	0.037
% H ₂ O	95.0
V _{total} (mL)	1.181
[VA-044]₀ (mol.L ⁻¹)	5 10 ⁻⁴
[NAM]₀ (mol.L ⁻¹)	3
[CTA] ₀ /[VA-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 H₂O/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-044 added} (mg)	0.191
V _{H2O added} (mL)	0.671
V _{dioxane added} (mL)	0.037
% H ₂ O	95.0
V _{total} (mL)	1.181
[VA-044]₀ (mol.L ⁻¹)	5 10 ⁻⁴
[NAM]₀ (mol.L ⁻¹)	3
[CTA] ₀ /[VA-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 PNAM₁₀*b*-PDMA₁₀-*b*-PNAM₁₀-*b*-PHEAm₁₀-*b*-PDEA₁₀ (Scheme 4, multiblock **h**) in H₂O/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				
$m_{VA-044 added} (mg)$	0.611	0.573	0.763	1.145	1.527
m _{VA-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 ₂ O	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-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-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

Table S9. Experimental conditions for the preparation of the pentablock copolymer $PNAM_{20}$ *b*-PDMA₂₀-*b*-PNAM₂₀-*b*-PHEAm₂₀-*b*-PDEA₂₀ (Scheme 4, multiblock i) in H₂O/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				
$m_{VA-044 added} (mg)$	0.458	0.458	0.611	1.018	1.145
m _{VA-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 ₂ O	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-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-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

Table S10. Experimental conditions for the preparation of the tetrablock copolymer PNAM₅₀-*b*-PDMA₅₀-*b*-PHEAm₅₀-*b*-PDEA₅₀ (Scheme 4, multiblock **j**) in H₂O/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			
$m_{VA-044 added} (mg)$	0.229	0.366	0.611	0.833
m _{VA-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 ₂ O	79.9	85.6	89.3	92.2
V _{total} ^[b] (mL)	0.810	1.325	1.893	2.601
[VA-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-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

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-044 added} (mg)	0.716	0.573	0.881
m _{VA-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 ₂ O	74.9	82.1	87.8
V _{total} ^[b] (mL)	1.012	1.603	2.466
[VA-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-044] ₀	80	67	51
L ^[c] (%)	99.3	98.9	98.6
Cumulative L ^[d] (%)	99.3	98.2	96.8

Table S11. Experimental conditions for the preparation of the triblock copolymer PNAM₂₀*b*-PDMA₂₀-*b*-PDEA₂₀ (Scheme 4, multiblock **k**) in H₂O/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		
$m_{VA-044 added} (mg)$	0.716	0.498	0.881
m _{VA-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 ₂ O	74.9	84.4	91.8
V _{total} ^[b] (mL)	1.012	1.721	2.902
[VA-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-044] ₀	80	73	52
L ^[c] (%)	99.3	99.0	98.6
Cumulative L ^[d] (%)	99.3	98.3	96.9

Table S12. Experimental conditions for the preparation of the triblock copolymer $PNAM_{20}$ *b*-PDMA₂₀-*b*-PHEAm₂₀ (Scheme 4, multiblock I) in H₂O/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-044 added} (mg)	0.229	0.382	0.674
m _{VA-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 ₂ O	95.1	96.5	97.2
V _{total} ^[b] (mL)	1.012	1.602	2.310
[VA-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-044] ₀	50	24	14
L ^[c] (%)	98.8	97.1	95.2
Cumulative L ^[d] (%)	98.8	96.0	91.3

Table S13. Experimental conditions for the preparation of the triblock copolymer PNAM₁₀₀*b*-PDMA₁₀₀-*b*-PDEA₁₀₀ (Scheme 4, multiblock **m**) in H₂O/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-044 added} (mg)	0.231	0.491
m _{VA-044 initial} ^[a] (mg)	0.231	0.583
V _{H2O} (mL)	0.510	0.781
V _{dioxane added} (mL)	0.057	0
% H ₂ O	89.9	95.8
V _{total} ^[b] (mL)	1.012	2.341
[VA-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-044] ₀	33	13
L ^[c] (%)	98.2	94.8
Cumulative L ^[d] (%)	98.2	93.1

Table S14. Experimental conditions for the preparation of the diblock copolymer PNAM₁₅₀*b*-PDMA₁₅₀ (Scheme 4, multiblock **n**) in H₂O/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-044 added} (mg)	0.229	0.636
m _{VA-044 initial} ^[a] (mg)	0.229	0.728
V _{H2O} (mL)	0.510	1.041
V _{dioxane added} (mL)	0.057	0
% H ₂ O	89.9	96.5
V _{total} ^[b] (mL)	1.012	2.783
[VA-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-044] ₀	25	8
L ^[c] (%)	96.2	88.7
Cumulative L ^[d] (%)	96.2	85.3

Table S15. Experimental conditions for the preparation of the diblock copolymer PNAM₂₀₀*b*-PDMA₂₀₀ (Scheme 4, multiblock **o**) in H₂O/dioxane at 100°C with VA-044 as initiator (3 min per block, in the presence of air, and without degassing).