

From One-Pot Stabilisation to In Situ Functionalisation in Nitroxide Mediated Polymerisation: An Efficient Extension towards Atom Transfer Radical Polymerisation

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SUPPORTING INFORMATION

Thiols

Table S1 Experiments for one-pot removal of nitroxides from NMP polymers with thiols^a.

Entry	M ^b	Initiation ^c	DP ^d	T (K)	Thiol	Eq. ^e	t _i – t _f ^f (min)	M _{n,i} – M _{n,f} ^g (g.mol ⁻¹)	PDI _i – PDI _f ^h
1	S	AIBN / SG1 (1 / 2)	412	393	1-dodecanethiol	1	180 – 240	33,300 – 12,700	1.21 – 2.81
2	MMA ⁱ	MAMA-SG1 ^j	244	363	1-dodecanethiol	10	120 – 180	12,100 – 2,900	1.51 – 3.87
3	MMA ⁱ	MAMA-SG1 ^j	240	363	thiophenol	10	120 – 180	13,600 – 5,000	1.41 – 3.33
4	iBA	MAMA-SG1 ^j	245	393	thiophenol	10	60 – 120	9,800 – 3,400	1.34 – 3.32
5	S	AIBN / TEMPO (1 / 2)	233	408	1-dodecanethiol	1	180 – 210	5,700 – 3,200	1.22 – 1.88

^a A typical reaction procedure is given below for entry 1. ^b M = monomer. ^c initiator / nitroxide molar ratio is given between brackets for bimolecular systems. ^d Theoretical degree of polymerisation at 100% conversion. ^e Thiol equivalents compared to the nitroxide. ^f t_i = thiol injection time; t_f = final reaction time. ^g M_{n,i} = molar mass just before thiol injection; M_{n,f} = molar mass at the end of the reaction. ^h PDI_i = PDI just before thiol injection; PDI_f = PDI at the end of the reaction. ⁱ 8.8 mol% of S was added to ensure control over the polymerisation. ^j 10 mol% of SG1 was added to improve control over the polymerisation.

1: NMP of styrene and nitroxide removal in the presence of 1-dodecanethiol

Styrene (3 mL, 2.61 x 10⁻² mol), SG1 (0.01713 g, 5.81 x 10⁻⁵ mol) and AIBN (0.00520 g, 3.17 x 10⁻⁵ mol) were introduced in a 5 mL glass vial equipped with a magnetic bar and stirred gently during 30 min. In another 1 mL vial, 0.15 mL of 1-dodecanethiol (0.12675 g, 6.27 x 10⁻⁴ mol, 10.8 equivalents with respect to SG1) was degassed under argon.

The mixture of monomer, SG1 and AIBN was then transferred into a Schlenk vessel and degassed by three freeze-pump-thaw cycles. Subsequently, the vessel was backfilled with nitrogen gas and the reaction mixture was immersed in an oil bath, which was preheated at 393 K (the pale red colour of the original reaction mixture disappeared in a few minutes). Time t_0 for the beginning of the reaction was arbitrary taken 5 min after immersion in the oil bath to allow for thermal equilibration. For kinetic analyses, samples were withdrawn from the reactor under nitrogen at 30 min intervals. The monomer conversion was determined by ^1H NMR analysis on crude samples dissolved in CDCl_3 . Molecular weights were determined by size exclusion chromatography (SEC).

After 180 min of reaction, a crude sample from the reaction mixture was cooled, diluted with THF and precipitated into an excess of methanol. Just after that, 1-dodecanethiol was added to the remaining reaction mixture and sampling was performed 10 min, 30 min and 1h after addition. The crude reaction mixture was cooled with ice, diluted with THF, and precipitated into an excess of chilled methanol. The resulting polymer was isolated by filtration and dried under vacuum (10^{-2} mmHg) at 298 K for 2 h to yield a dry powder.

2: NMP of MMA and nitroxide removal in the presence of 1-dodecanethiol

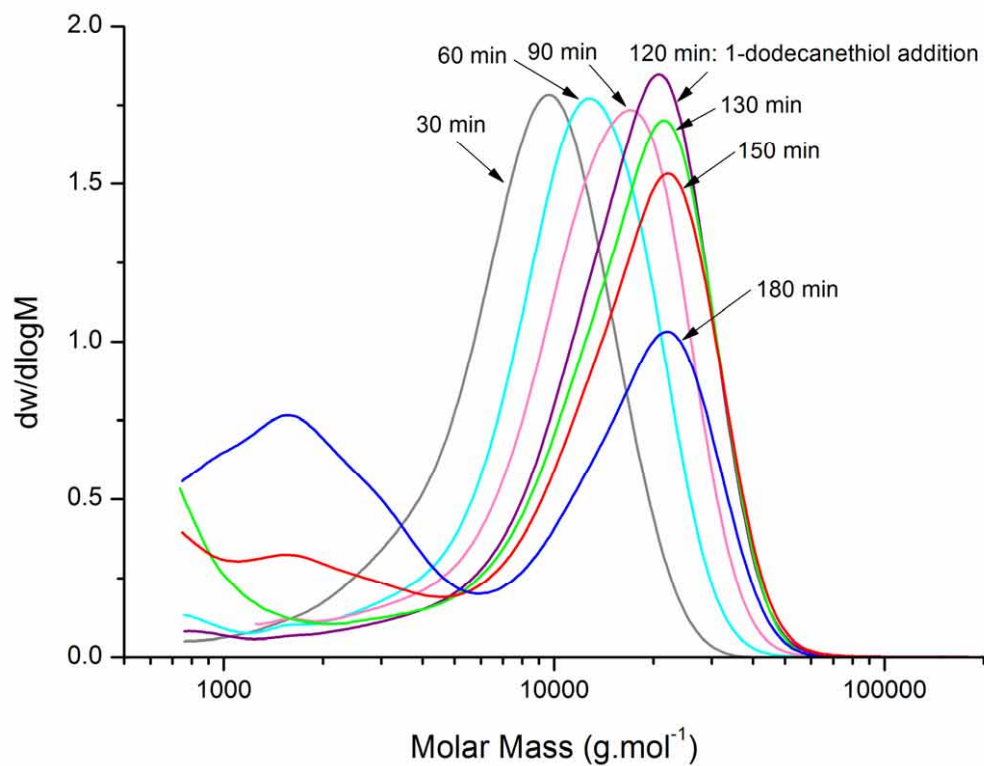


Figure S1 Evolution of molar mass distribution for PMMA synthesised by NMP and one-pot SG1 removal with 1-dodecanethiol (entry 2, Table S1).

3: NMP of MMA and nitroxide removal in the presence of thiophenol

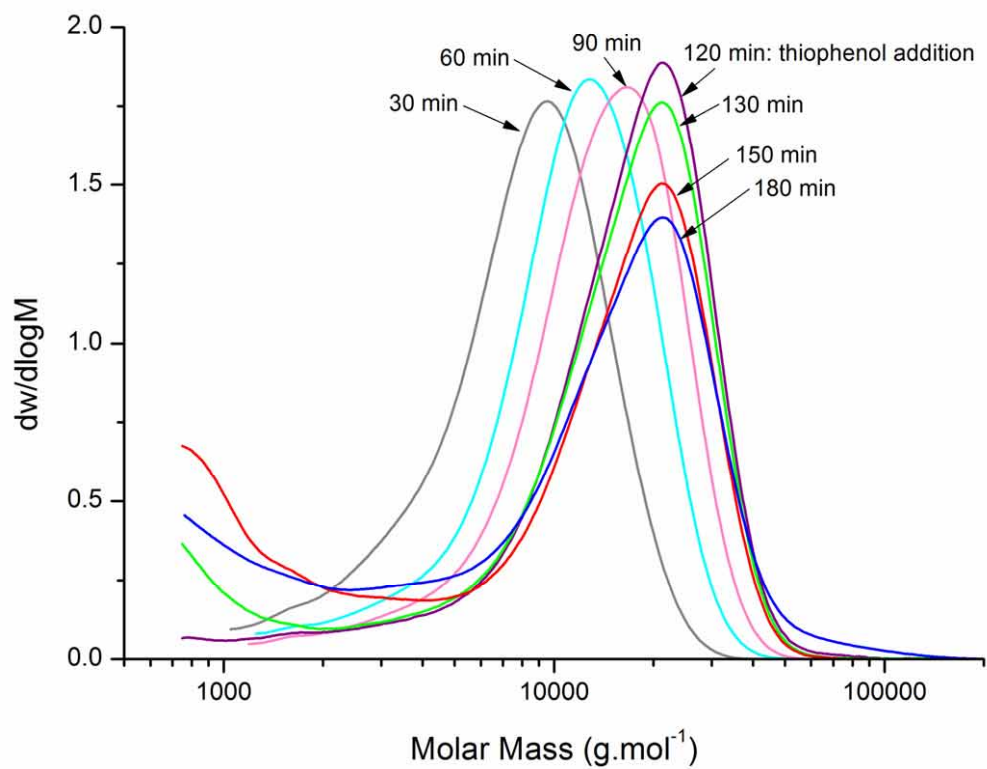


Figure S2 Evolution of molar mass distribution for PMMA synthesised by NMP and one-pot SG1 removal with thiophenol (entry 3, Table S1).

4: NMP of iBA and nitroxide removal in the presence of thiophenol

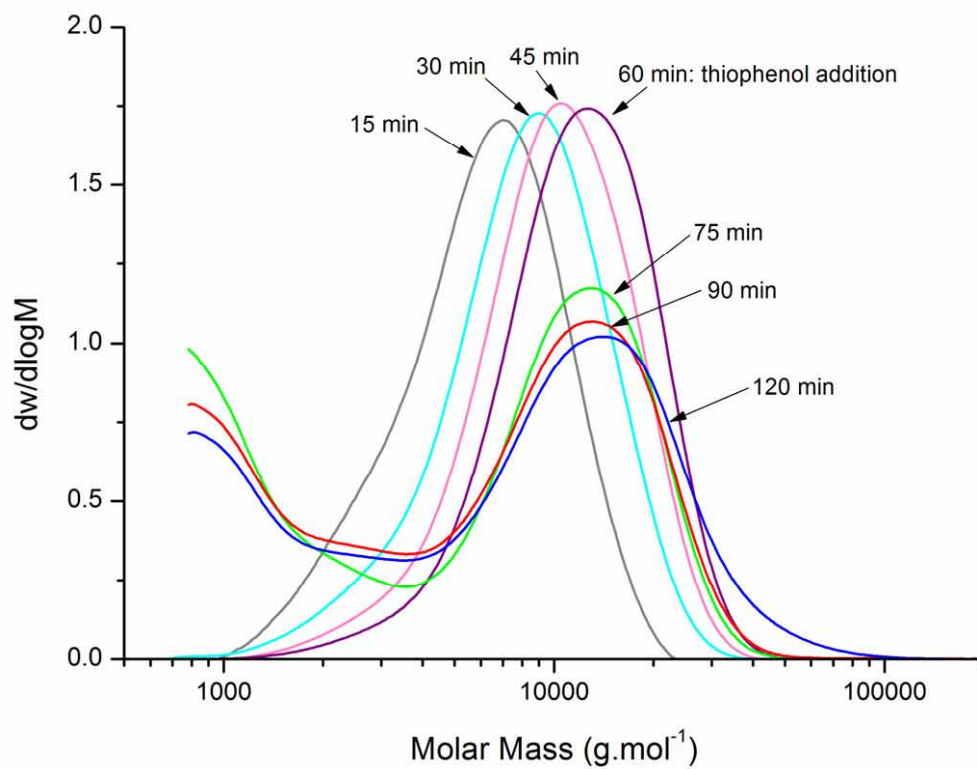


Figure S3 Evolution of molar mass distribution for PiBA synthesised by NMP and one-pot SG1 removal with thiophenol (entry 4, Table S1).

5: NMP of styrene and nitroxide removal in the presence of 1-dodecanethiol

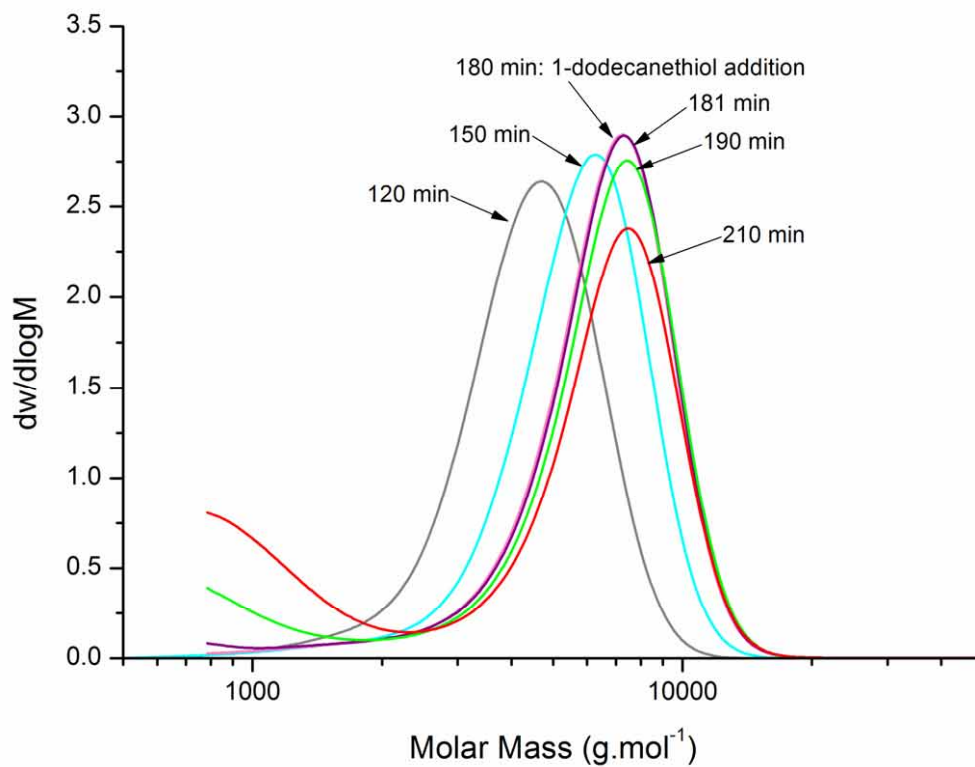


Figure S4 Evolution of molar mass distribution for PS synthesised by NMP and one-pot TEMPO removal with 1-dodecanethiol (entry 5, Table S1).

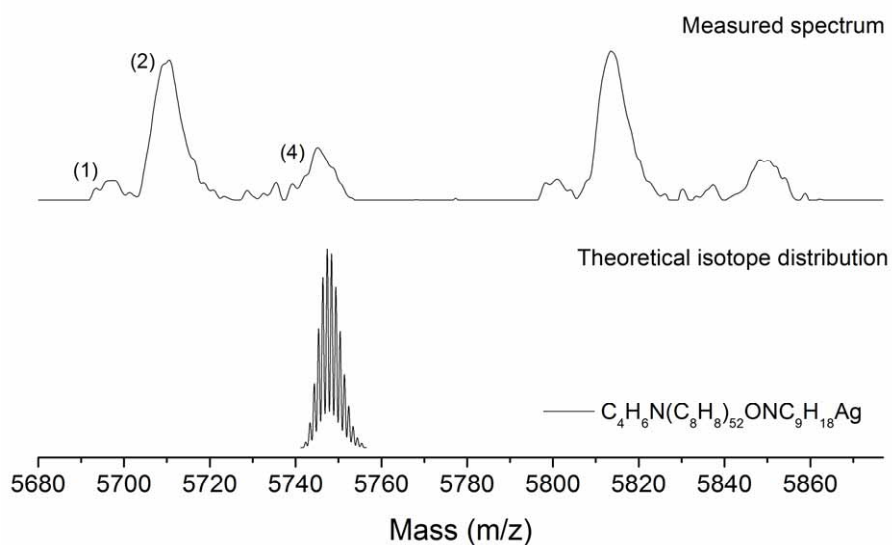


Figure S5 Comparison of measured MALDI-TOF spectrum of entry 5 in Table S1 before the addition of 1-dodecanethiol (top) and theoretical isotope distribution of $C_4H_6N(C_8H_8)_{52}ONC_9H_{18}Ag$ (bottom).

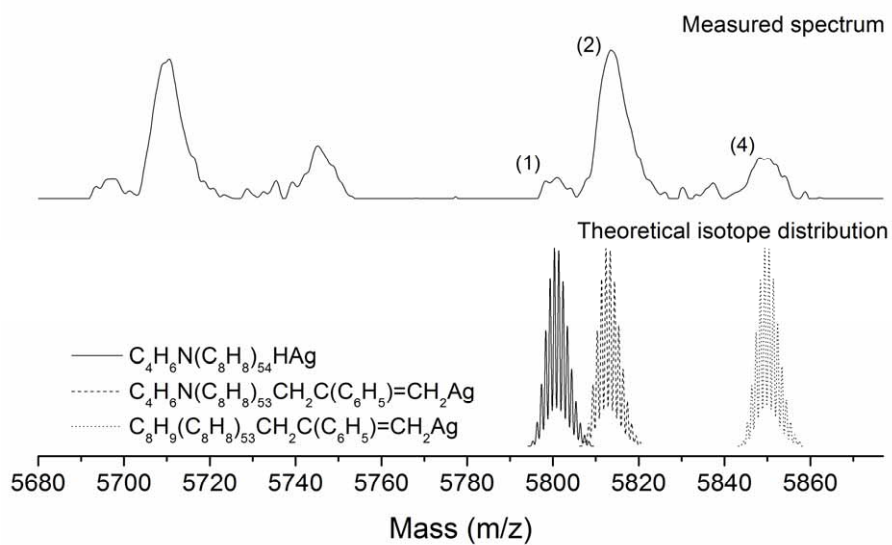


Figure S6 Comparison of measured MALDI-TOF spectrum of entry 5 in Table S1 before the addition of 1-dodecanethiol (top) and theoretical isotope distribution of $C_4H_6N(C_8H_8)_{54}HAg$, $C_4H_6N(C_8H_8)_{53}CH_2C(C_6H_5)=CH_2Ag$, and $C_8H_9(C_8H_8)_{53}CH_2C(C_6H_5)=CH_2Ag$ (bottom).

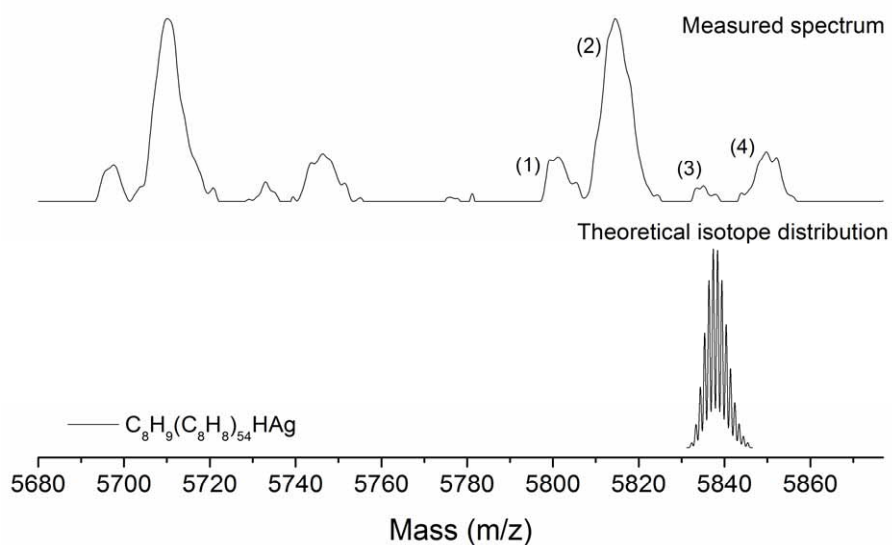


Figure S7 Comparison of measured MALDI-TOF spectrum of entry 5 in Table S1 1 min after the addition of 1-dodecanethiol (top) and theoretical isotope distribution of $C_8H_9(C_8H_8)_{54}HAg$ (bottom).

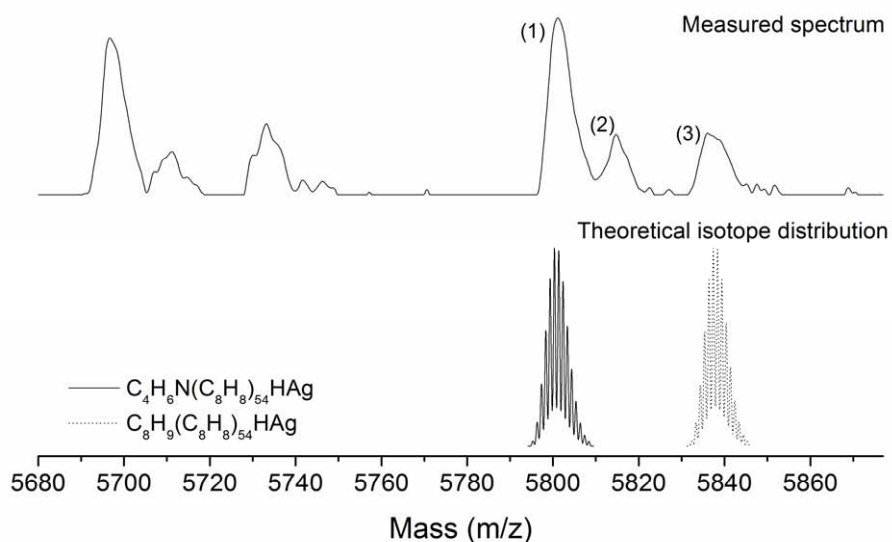


Figure S8 Comparison of measured MALDI-TOF spectrum of entry 5 in Table S1 10 min after the addition of 1-dodecanethiol (top) and theoretical isotope distribution of $C_4H_6N(C_8H_8)_{54}HAg$, and $C_8H_9(C_8H_8)_{54}HAg$ (bottom).

Remark on the theoretical isotope distributions of thermally initiated polymers that only one of the two distributions has been simulated. The other series that is 2 Da lower has not been presented.

Radical Initiators

Table S2 Experiments for one-pot removal of nitroxides from NMP polymers with radical sources^a.

Entry	DP ^b	Radical Source	Eq. ^c	$t_i - t_f^d$ (min)	$M_{n,i} - M_{n,f}^e$ (g.mol ⁻¹)	PDI _i - PDI _f ^f
6	446	BPO	10	180 – 240	33,300 – 5,000	1.23 – 5.32
7	476	AIBN	10	180 – 240	31,500 – 6,500	1.23 – 4.33
8	446	AIBN	2	180 – 240	34,800 – 20,100	1.27 – 2.18
9	443	AIBN	4	180 – 240	38,000 – 15,300	1.28 – 2.76
10	428	AIBN	10	900 – 1440	55,400 – 60,700	1.49 – 1.41
11 ^g	379	AIBN	10	900 – 1440	41,900 – 36,200	1.74 – 1.74

^a Monomer: styrene; initiation: AIBN / SG1 (molar ratio = 1 / 2); temperature: 393 K (A typical reaction procedure is given below for entry 6). ^b Theoretical degree of polymerisation at 100% conversion. ^c Radical source equivalents compared to the nitroxide. ^d t_i = radical source injection time; t_f = final reaction time. ^e $M_{n,i}$ = molar mass just before radical source injection; $M_{n,f}$ = molar mass at the end of the reaction. ^f PDI_i = PDI just before radical source injection; PDI_f = PDI at the end of the reaction. ^g 50 vol% of *o*-xylene was also added.

6: NMP of styrene and nitroxide removal in the presence of BPO

Styrene (3 mL, 2.61×10^{-2} mol), SG1 (0.01676 g, 5.68×10^{-5} mol), and AIBN (0.00450 g, 2.74×10^{-5} mol) were introduced in a 5 mL glass vial equipped with a magnetic bar and stirred gently during 30 min. In another 1 mL vial, 0.17717 g of BPO (5.49×10^{-4} mol, 9.66 equivalents with respect to SG1) were dissolved in a minimal amount of *o*-xylene necessary for complete dissolution of BPO and the solution was degassed under argon.

The mixture of monomer, SG1 and BPO was then transferred into a Schlenk vessel and degassed by three freeze-pump-thaw cycles. Subsequently, the vessel was backfilled with nitrogen gas and the reaction mixture was immersed in an oil bath, which was preheated at 393 K (the pale red colour of the original reaction mixture disappeared in a few minutes). Time t_0 for the beginning of the reaction was arbitrary taken 5 min after immersion in the oil bath to allow for thermal equilibration. For kinetic analyses, samples were withdrawn from the reactor under nitrogen at 30 min intervals. The monomer conversion was determined by ¹H NMR analysis on crude samples dissolved in CDCl₃. Molecular weights were determined by size exclusion chromatography (SEC).

After 180 min of reaction, a crude sample from the reaction mixture was cooled, diluted with THF and precipitated into an excess of methanol. Just after that, the BPO

solution was added to the remaining reaction mixture and sampling was performed 10 min, 30 min and 1h after addition. A highly viscous media was observed 40 min after BPO addition. The crude reaction mixture was cooled with ice, diluted with THF and precipitated into an excess of chilled methanol. The resulting polymer was isolated by filtration and dried under vacuum (10^{-2} mmHg) at 298 K for 2 h to yield a dry powder.

7: NMP of styrene and nitroxide removal in the presence of AIBN

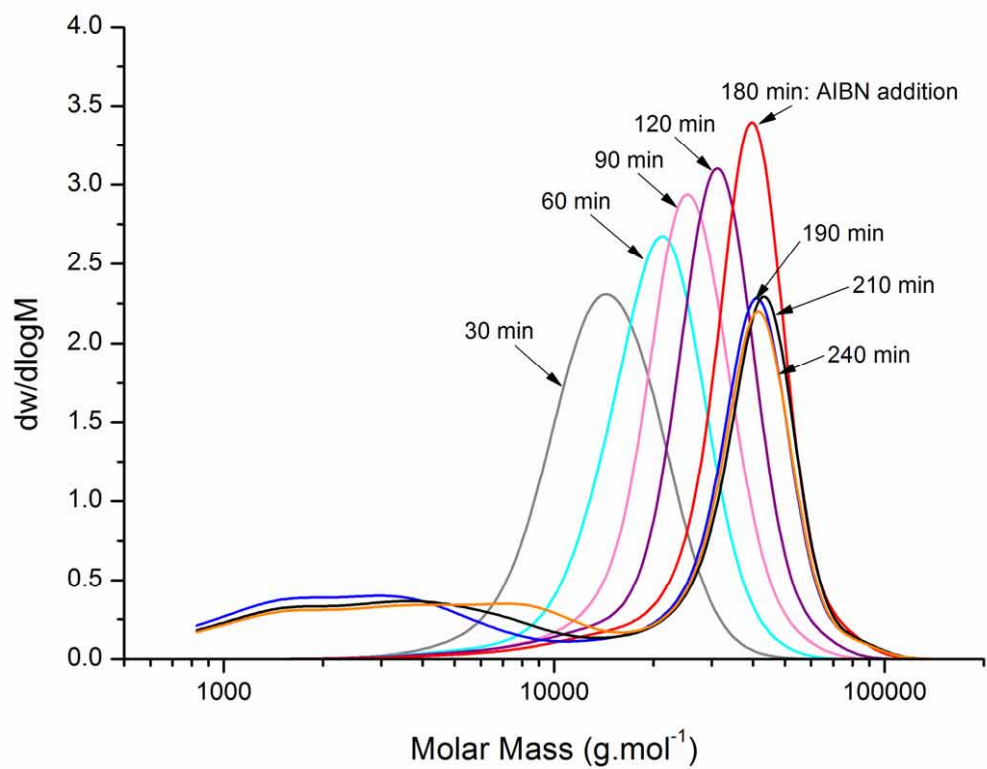


Figure S9 Evolution of molar mass distribution for PS synthesised by NMP and one-pot SG1 removal with AIBN (entry 7, Table S2).

8: NMP of styrene and nitroxide removal in the presence of AIBN

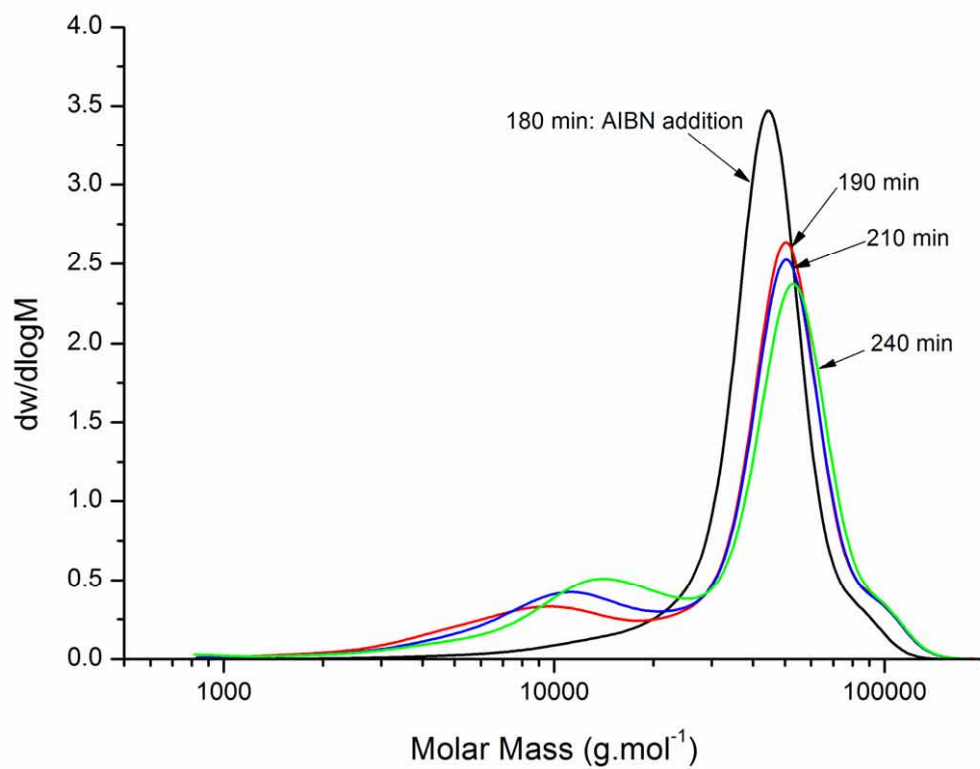


Figure S10 Evolution of molar mass distribution for PS synthesised by NMP and one-pot SG1 removal with AIBN (entry 8, Table S2).

9: NMP of styrene and nitroxide removal in the presence of AIBN

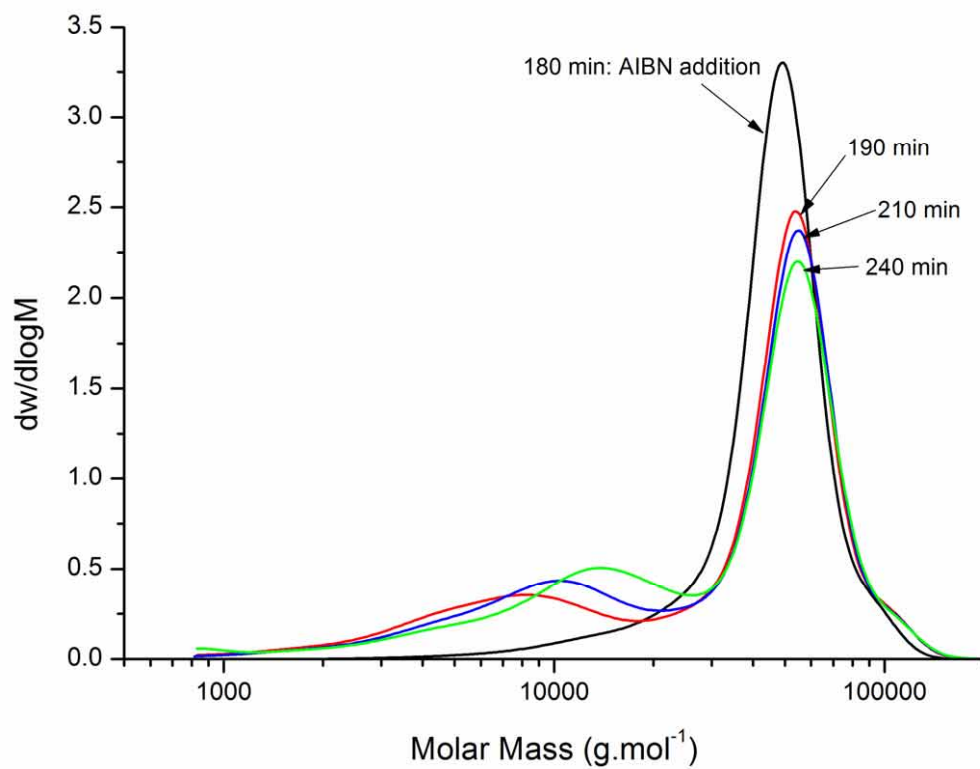


Figure S11 Evolution of molar mass distribution for PS synthesised by NMP and one-pot SG1 removal with AIBN (entry 9, Table S2).

11: NMP of styrene and nitroxide removal in the presence of AIBN

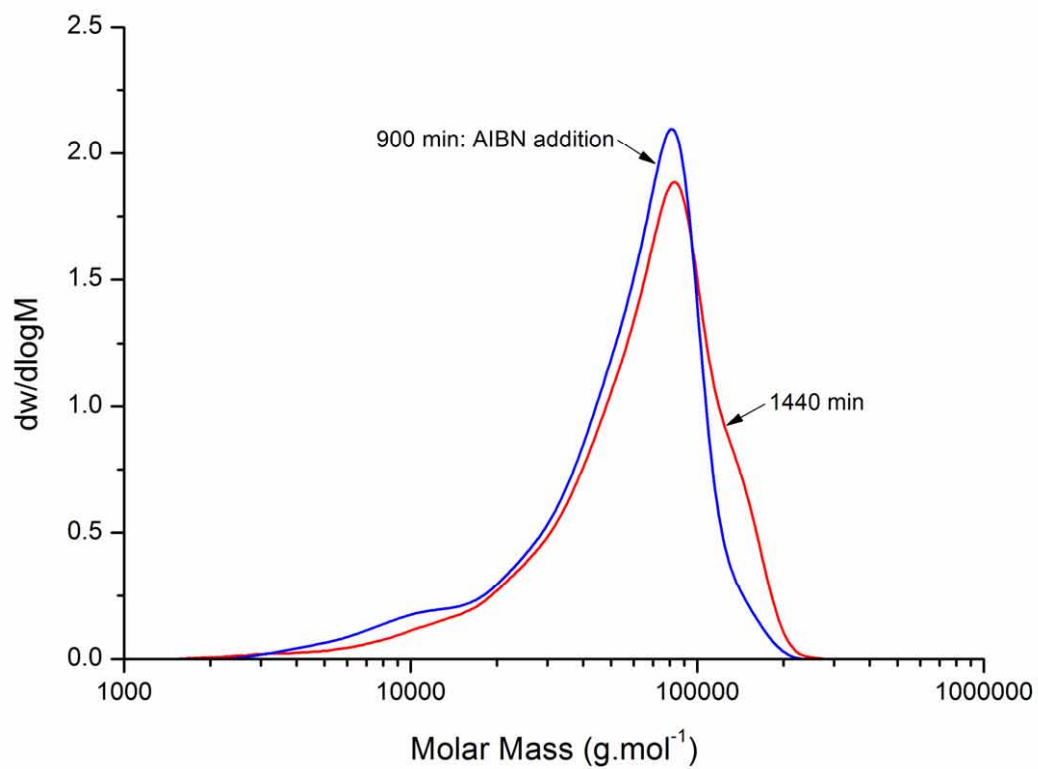


Figure S12 Evolution of molar mass distribution for PS synthesised by NMP and one-pot SG1 removal with AIBN (entry 11, Table S2).

Halogen: CBr₄

Table S3 Experiments for one-pot removal of nitroxides from NMP polymers with CBr₄^a.

Entry	M ^b	Initiation ^c	DP ^d	T (K)	CBr ₄ Eq. ^e	t _i – t _f ^f (min)	M _{n,i} – M _{n,f} ^g (g.mol ⁻¹)	PDI _i – PDI _f ^h
12	S	AIBN / SG1 (1 / 2)	468	393	10	180 – 240	32,300 – 25,600	1.24 – 1.58
13	S	AIBN / SG1 (1 / 2)	95	393	1	180 – 190	9,400 – 9,500	1.19 – 1.20
14	S	AIBN / SG1 (1 / 3)	71	393	1	240 – 250	3,500 – 3,600	1.11 – 1.18
15	iBA	AIBN / SG1 (1 / 2)	49	393	1	360 – 370	4,700 – 5,200	1.15 – 1.10
16	MMA ⁱ	MAMA-SG1 ^j	86	363	1	120 – 130	5,700 – 4,900	1.30 – 1.51

^a A typical reaction procedure is given below for 12. ^b M = monomer. ^c initiator / nitroxide molar ratio is given between brackets for bimolecular systems. ^d Theoretical degree of polymerisation at 100% conversion. ^e CBr₄ equivalents compared to the nitroxide. ^f t_i = CBr₄ injection time; t_f = final reaction time. ^g M_{n,i} = molar mass just before CBr₄ injection; M_{n,f} = molar mass at the end of the reaction. ^h PDI_i = conversion just before CBr₄ injection; PDI_f = conversion at the end of the reaction. ⁱ 8.8 mol% of S was added to ensure control over the polymerisation. ^j 10 mol% of SG1 was added to improve control over the polymerisation.

Remark: MALDI-TOF analysis was not performed on the end-products due to the weakness of the C-Br bond, which tend to be cleaved easily (N. K. Singha, S. Rimmer and B. Klumperman, *Eur. Polym. J.*, 2004, **40**, 159-163).

12: NMP of styrene and nitroxide removal in the presence of CBr₄

Styrene (3 mL, 2.61 x 10⁻² mol), SG1 (0.01602 g, 5.43 x 10⁻⁵ mol) and AIBN (0.00457 g, 2.79 x 10⁻⁵ mol) were introduced in a 5 mL glass vial equipped with a magnetic bar and stirred gently during 30 min. In another 1 mL vial, 0.18058 g of CBr₄ (5.44 x 10⁻⁴ mol, 10 equivalents with respect to SG1) were dissolved in 0.2 mL of *o*-xylene and degassed under argon.

The mixture of monomer, SG1 and AIBN was then transferred into a Schlenk vessel and degassed by three freeze-pump-thaw cycles. Subsequently, the vessel was backfilled with nitrogen gas and the reaction mixture was immersed in an oil bath, which was pre-heated at 393 K (the pale red colour of the original reaction mixture disappeared in a few minutes). Time t₀ for the beginning of the reaction was arbitrary taken 5 min after immersion in the oil bath to allow for thermal equilibration. For kinetic analyses, samples were withdrawn from the reactor under nitrogen at 30 min intervals. The monomer conversion was determined by ¹H NMR analysis on crude samples dissolved in CDCl₃. Molecular weights were determined by size exclusion chromatography (SEC).

After 180 min of reaction, a crude sample from the reaction mixture was cooled, diluted with THF and precipitated into an excess of methanol. After that, the CBr_4 solution was added to the remaining reaction mixture and sampling was performed 10 min, 30 min and 1h after addition. After the CBr_4 addition the reaction mixture became pale yellow and turned brown at the end of the reaction. The crude reaction mixture was cooled with ice, diluted with THF and precipitated into an excess of chilled methanol. The resulting polymer was isolated by filtration and dried under vacuum (10^{-2} mmHg) at 298 K for 2 h to yield a dry powder.

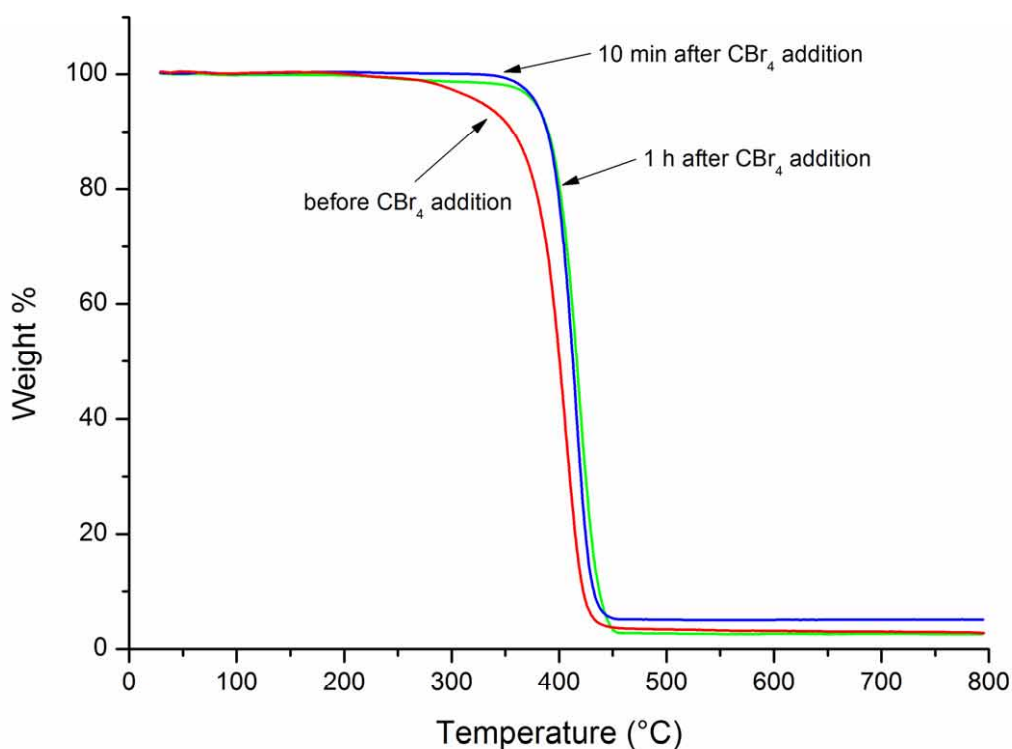


Figure S13 TGA before, 10 min and 1h after CBr_4 addition for PS synthesised with SG1 (entry 12, Table S3).

13: NMP of styrene and nitroxide removal in the presence of CBr₄

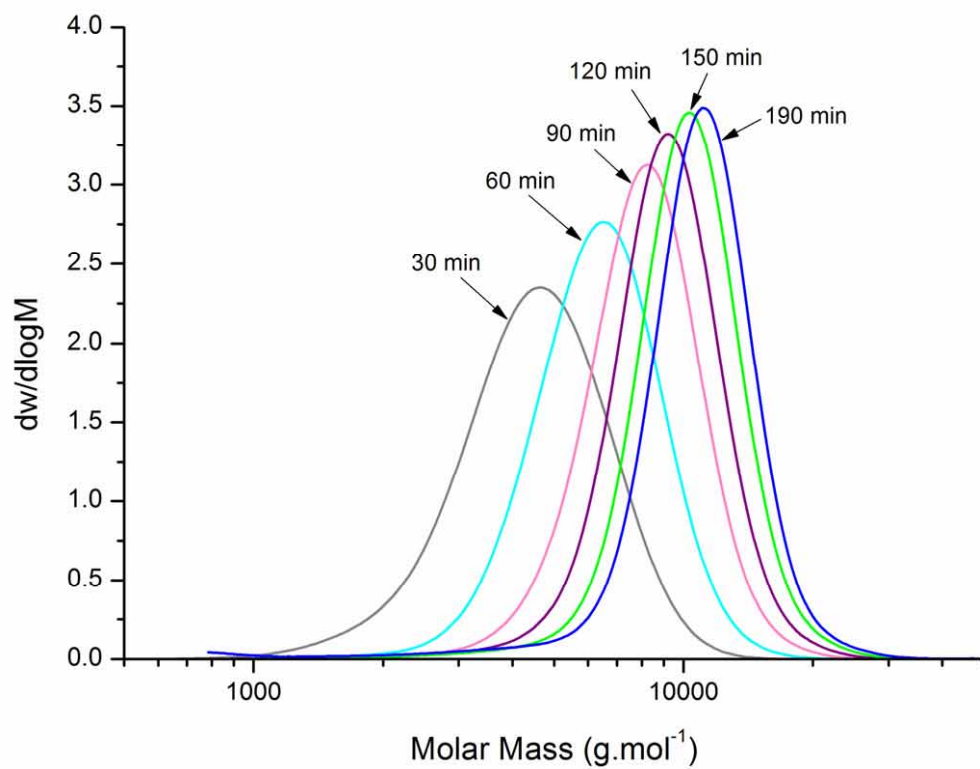


Figure S14 Evolution of molar mass distribution for PS synthesised by NMP and one-pot SG1 removal with CBr₄ (entry 13, Table S3). Trace at 180 min corresponding to CBr₄ addition is not shown here.

14: NMP of styrene and nitroxide removal in the presence of CBr_4

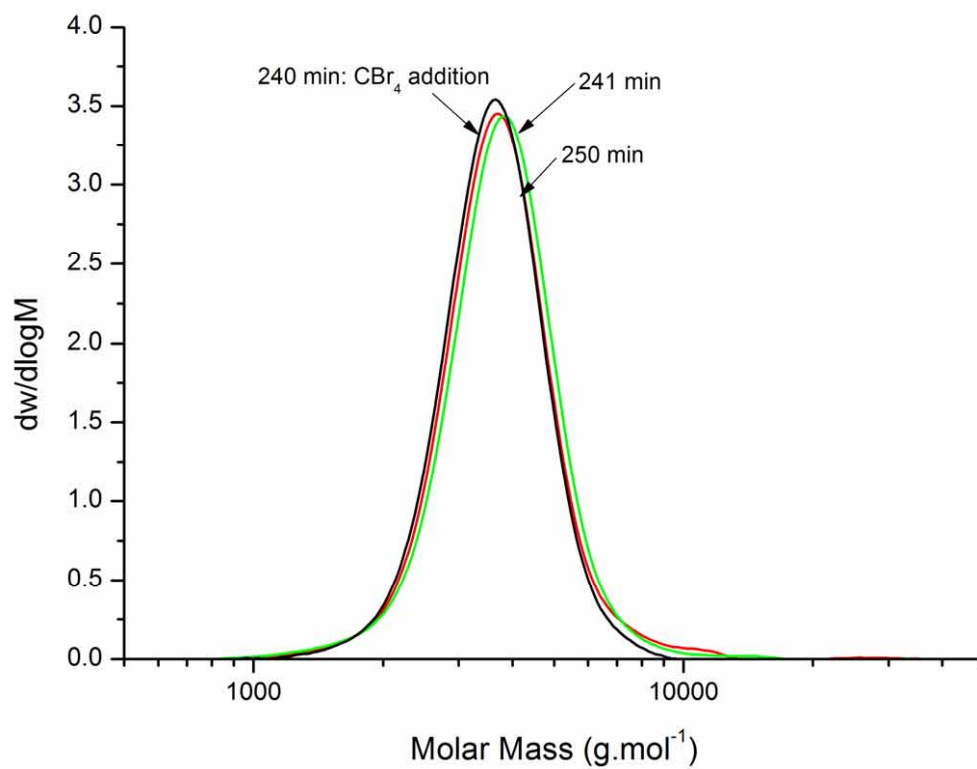


Figure S15 Evolution of molar mass distribution for PS synthesised by NMP and one-pot SG1 removal with CBr_4 (entry 14, Table S3).

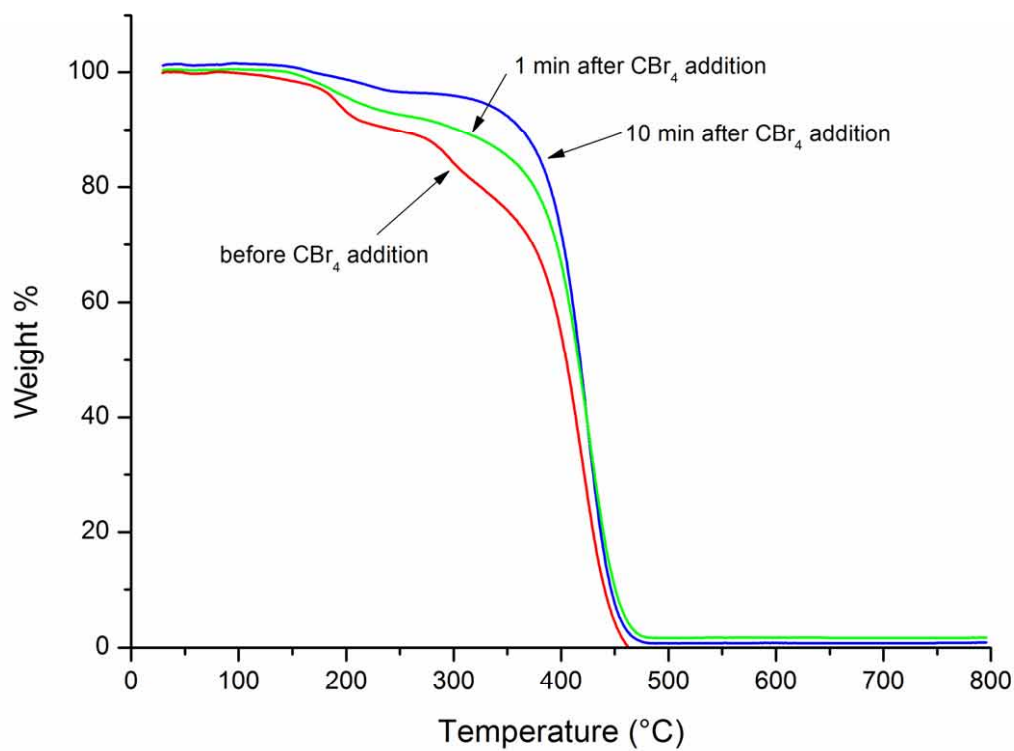


Figure S16 TGA before, 1 min and 10 min after CBr₄ addition for PS synthesised with SG1 (entry 14, Table S3).

15: NMP of iBA and nitroxide removal in the presence of CBr₄

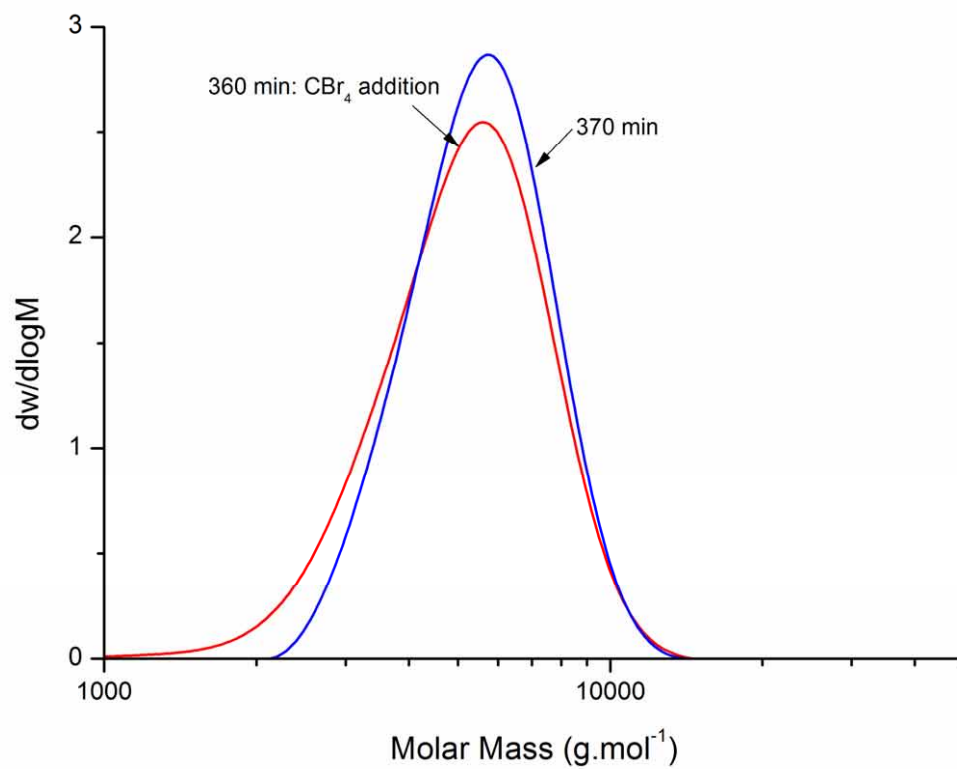


Figure S17 Evolution of molar mass distribution for PiBA synthesised by NMP and one-pot SG1 removal with CBr₄ (entry 15, Table S3).

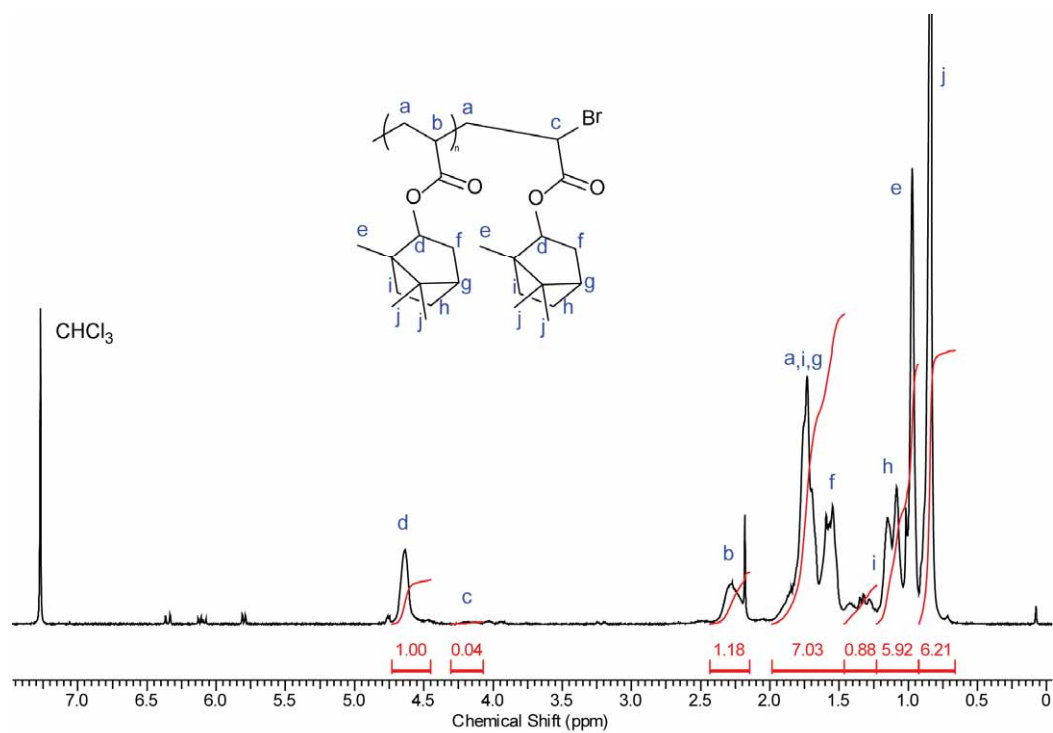


Figure S18 ¹H NMR (500 MHz) for PiBA-Br 10 min after CBr₄ addition (entry 15, Table S3).

16: NMP of MMA and nitroxide removal in the presence of CBr₄

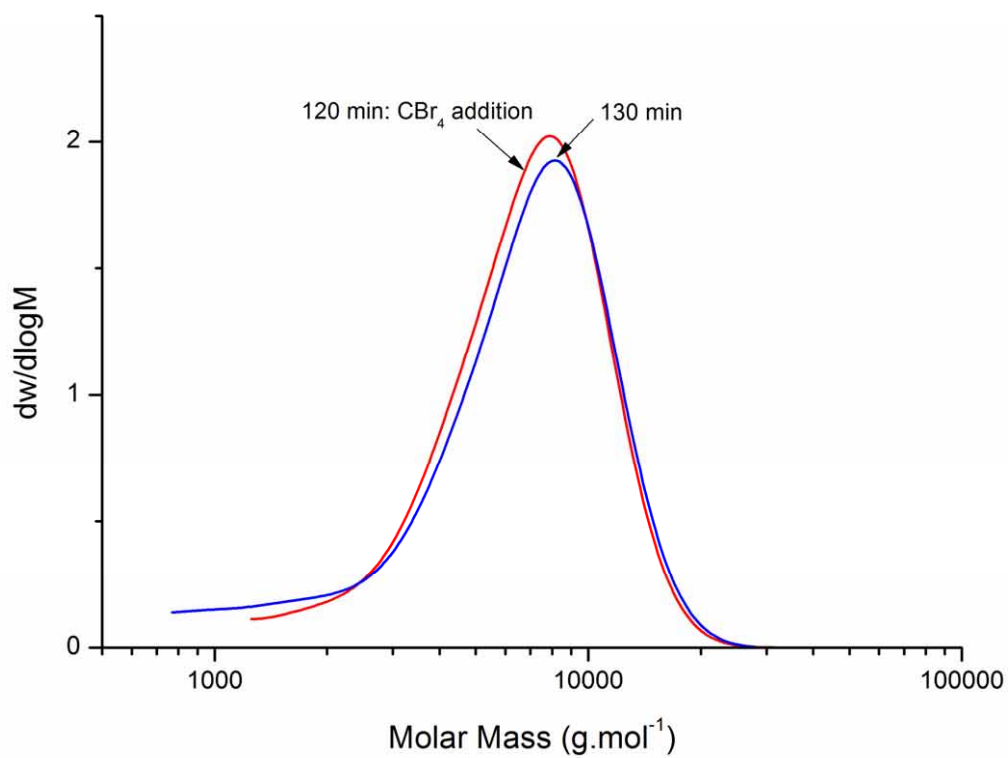


Figure S19 Evolution of molar mass distribution for PMMA synthesised by NMP and one-pot SG1 removal with CBr₄ (entry 16, Table S3).

Chain Extension by ATRP

Table S4 Chain extension by ATRP with bromine terminated macroinitiators^a.

Entry	MI ^b	M ^c	[M] ₀ /[MI]/[Cu(I)Br]/ [PMDETA]	T (K)	t (min)	M _{n,i} ^d (g.mol ⁻¹)	PDI ^d	M _{n,f} ^e (g.mol ⁻¹)	PDI ^e	Conv ^f (%)
17	PS-Br (entry 13)	S	300/1/1/1	383	360	10,000	1.07	25,300	1.18	57.2
18	PS-Br (entry 14)	S	300/1/1/1	383	360	3,800	1.06	21,200	1.31	-
19	PiBA-Br (entry 15)	iBA	300/1/1.5/1.5	348	1260	5,200	1.12	7,000	1.21	-
20	PMMA-Br (entry 16)	MMA	300/1/1/1	363	240	8,400	1.20	30,200	2.12	-
21	PMMA-Br (entry 16)	MMA	300/1/0.5/0.5	363	240	8,600	1.17	28,600	2.12	-

^a A typical reaction procedure is given below for entry 17. ^b MI = macroinitiator. ^c M = monomer. ^d Molar mass and PDI of the macroinitiator. ^e Molar mass and PDI after chain extension. ^f - = not determined.

17: Chain extension of PS-Br (entry 13, Table S3) by ATRP

PS-Br (0.30068 g, 2.91×10^{-5} mol), styrene (1 mL, 8.70×10^{-3} mol), and PMDETA (6 μ L, 2.90×10^{-5} mol) were mixed and stirred during 30 min in order to dissolve the PS-Br macroinitiator in the monomer. Then, the mixture was transferred to the Schlenk reactor and degassed by three freeze-pump-thaw cycles. Subsequently, it was backfilled with nitrogen and Cu(I)Br (0.00440 g, 3.06×10^{-5} mol) was added under a smooth nitrogen flow. The initial colourless mixture turned pale green after the addition of Cu(I)Br. One aliquot of this mixture was taken for analysis and the reaction flask was placed in an oil bath set at 383 K. Samples were withdrawn from the reaction system at 1 h intervals in order to determine the conversion and the polymer properties. The samples were dissolved in THF in order to perform SEC analysis. After 6 h, the ATRP experiment was terminated by quenching the reaction mixture with liquid nitrogen. After dissolution in THF, passing over a neutral aluminium oxide column to remove copper and evaporation of the solvent, the polymer was precipitated in a 10-fold excess of methanol.

18: Chain extension of PS-Br (entry 14, Table S3) by ATRP

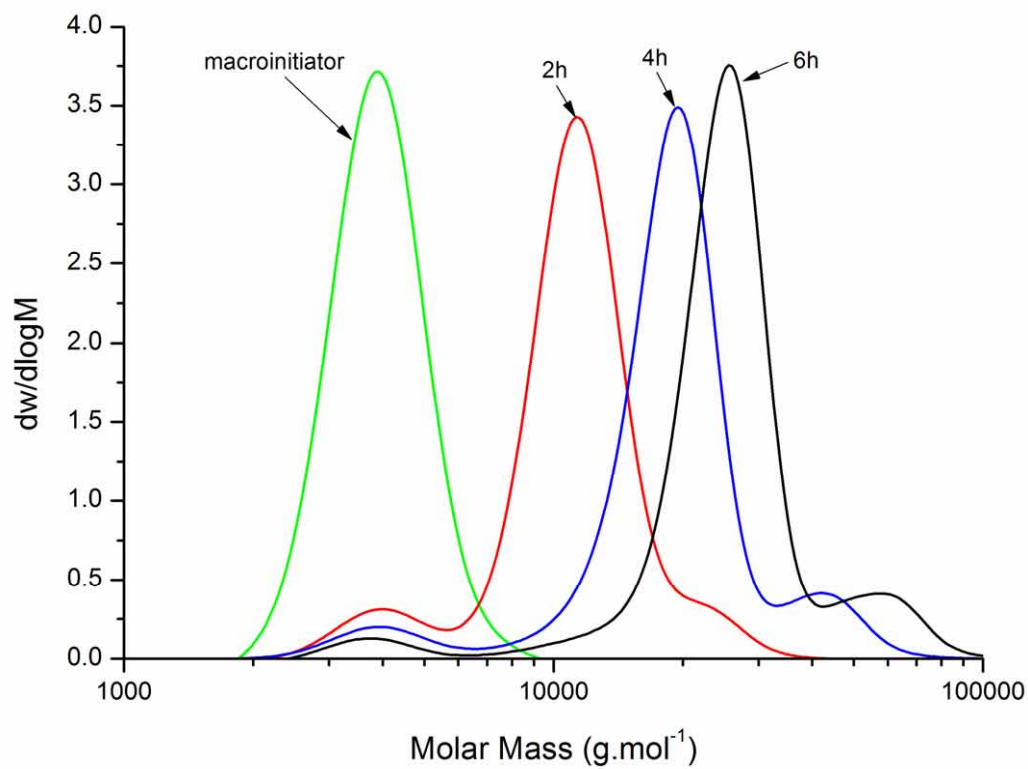


Figure S20 Molar mass distribution before and 2h, 4h and 6h after chain extension of a PS-Br macroinitiator by ATRP (entry 18, Table S4).

19: Chain extension of PiBA-Br (entry 15, Table S3) by ATRP

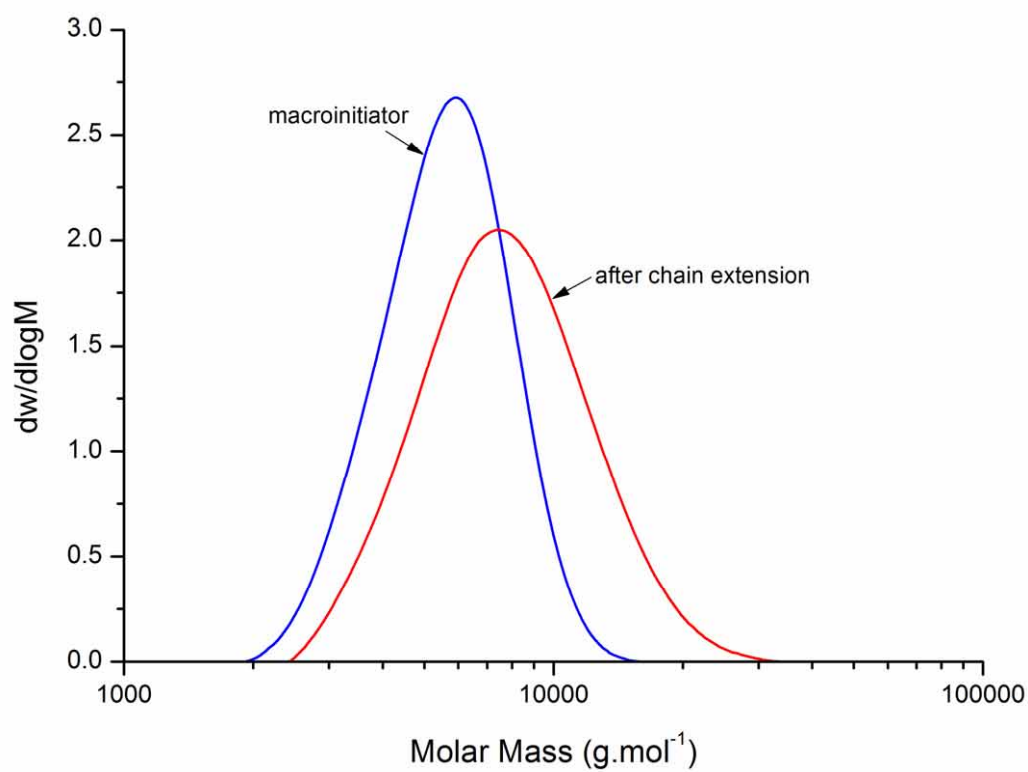


Figure S21 Molar mass distribution before (left) and after (right) chain extension of a PiBA-Br macroinitiator by ATRP (entry 19, Table S4).

20: Chain extension of PMMA-Br (entry 16, Table S3) by ATRP

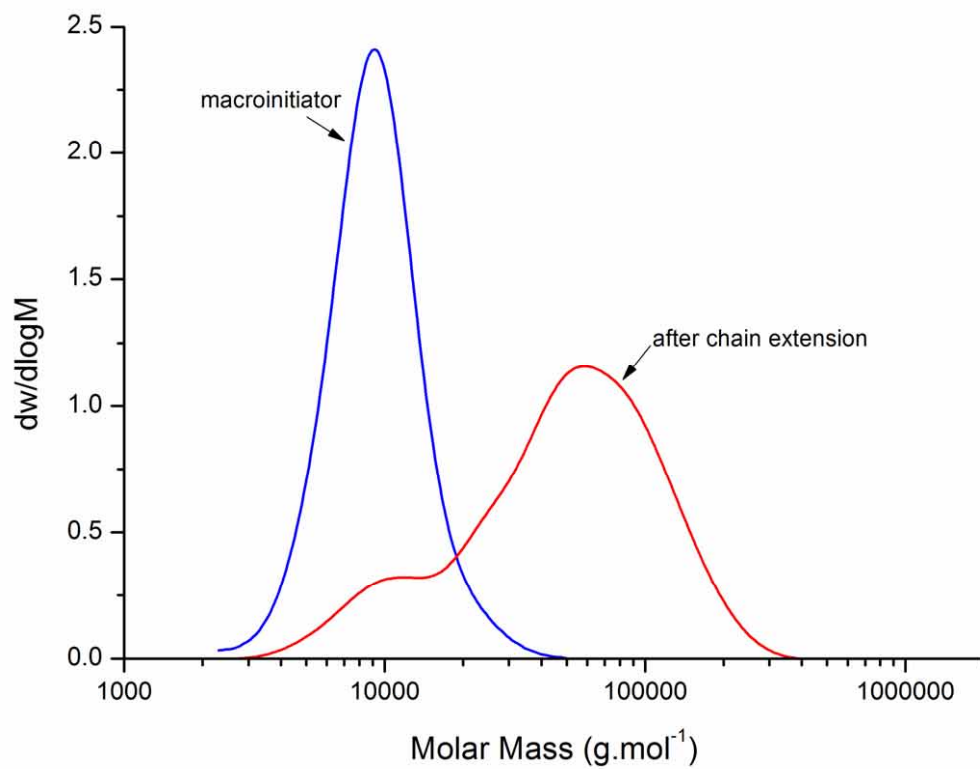


Figure S22 Molar mass distribution before (left) and after (right) chain extension of a PMMA-Br macroinitiator by ATRP (entry 20, Table S4).

21: Chain extension of PMMA-Br (entry 16, Table S3) by ATRP

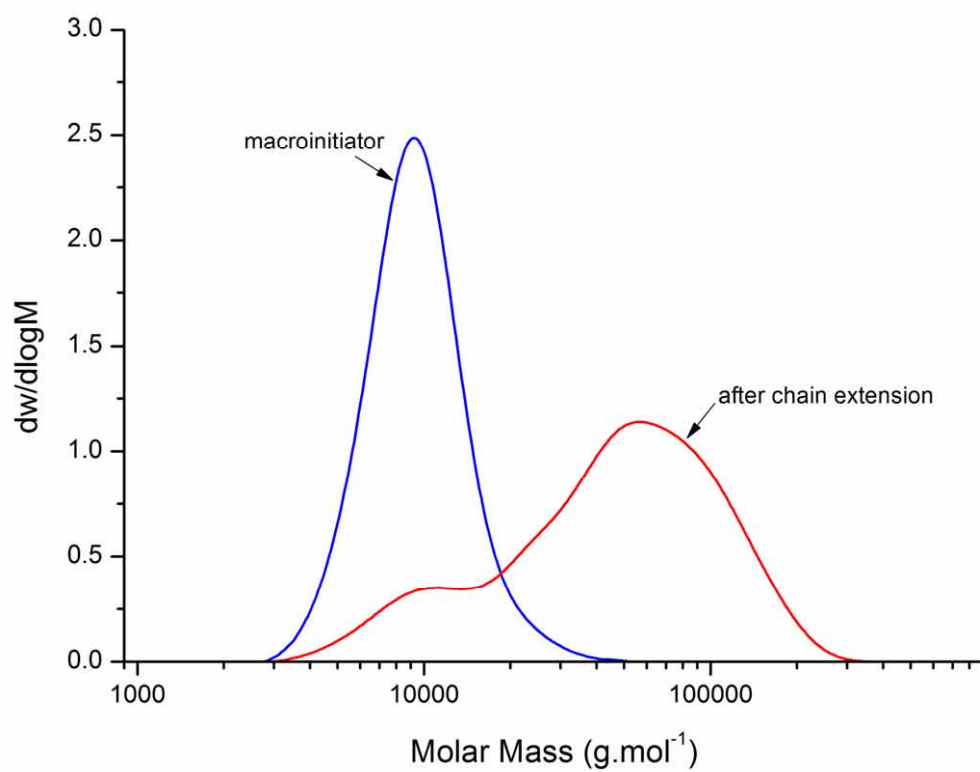


Figure S23 Molar mass distribution before (left) and after (right) chain extension of a PMMA-Br macroinitiator by ATRP (entry 21, Table S4).