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Authors Petton, L;, Ciolino, A.E., Dervaux B., Du Prez F.E.

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

Lionel Petton, Andrés E. Ciolino, Bart Dervaux, and Filip E. Du Prez*

Polymer Chemistry Research Group, Department of Organic Chemistry, Ghent University, Krijgslaan 281 S4 9000 Gent (Belgium),

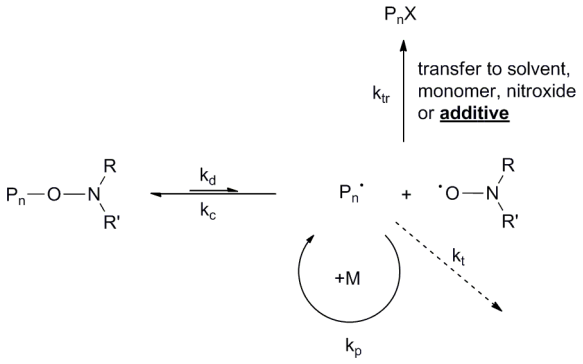
E-mail: Filip.DuPrez@UGent.be

ABSTRACT: A one-pot, controlled method for the nitroxide end-group removal from synthetic polymers prepared by nitroxide mediated radical polymerisation (NMP) is reported. The strategy relies on the controlled addition of compounds such as thiols, radical initiators and carbon tetrabromide with high chain transfer constants. From a practical point of view, when the desired molar mass and conversion is reached, 1 to 10 equivalents of the transfer agent compared to the nitroxide are added and a few minutes later, after transformation of all chain-ends, the reaction is quenched. The versatility of the procedure was successfully tested with a wide range of monomers (styrene (S), isobornyl acrylate (iBA) or methyl methacrylate (MMA)) and nitroxides (2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) and N-*tert*-butyl-1-diethylphosphono-2,2-dimethylpropyl nitroxide (SG1)). The removal of the nitroxide end-group proceeds with high fidelity for all the transfer agents studied, while at the same time the thermal stability of the resulting polymer chains increases when thiols are employed. Furthermore, a functional group that allows for chain extension by atom transfer radical polymerisation (ATRP) has been introduced through the direct synthesis of bromine terminated macroinitiators via a chain transfer reaction with carbon tetrabromide.

INTRODUCTION

The development of controlled radical polymerisation techniques, such as nitroxide mediated polymerisation (NMP)[1], atom transfer radical polymerisation (ATRP)[2], and reversible addition-fragmentation chain transfer polymerisation (RAFT)[3], allows for the structural control of vinyl polymers as well as a much easier access to complex macromolecular architectures[4]. In addition, these controlled techniques yield polymers with polydispersity indexes similar to those obtained by ionic polymerisation methods without the need for their stringent reaction conditions[5].

In many respects, all of the controlled free radical techniques are similar in their overall scope, although there are a number of subtle differences, which affect the applicability and suitability of each system for specific applications. For example, NMP[6] is easier than RAFT polymerisation[7] from a mechanistic point of view, while it has the advantage, compared to ATRP, that metal complexes are not necessary. Furthermore, NMP allows for the synthesis of colourless materials without the need for sophisticated purification. Its tolerance to functional groups and applicability to aqueous dispersed media[8] also make the technique interesting for a wide range of applications. Originally, the applicability of NMP was limited to styrenic monomers[9]. Nevertheless, this technique has witnessed important progress during the last 15 years, mainly thanks to the development of novel nitroxides[10] and alkoxyamines[11, 12] , which allowed for the polymerisation of other monomer classes such as acrylates[13], methacrylates under specific conditions[14], acrylamides[15], acrylonitrile[11], and even 1,3-dienes[16] as well as the design of complex macromolecular architectures[11, 17, 18] and advanced functional materials[19].



Scheme 1 Mechanism of nitroxide mediated polymerisation.

The unprecedented control in NMP is ascribed to the reversible termination of the growing polymeric radical by the stable nitroxide free radical[20] (Scheme 1). This process is based on the equilibrium between dormant species, in which the nitroxide is covalently bound to the polymer chain-end, and active species, $P_n^{\cdot}$, in which the nitroxide is homolytically cleaved to generate a propagating radical at the polymer chain-end. The activation–deactivation equilibrium constant K ($K = k_d/k_c$) is a critical parameter for an efficient and controlled polymerisation[21]. Below a threshold temperature, which depends on the nitroxide and monomer (M) used, K is too low for propagation to occur and the

nitroxide can be regarded as a radical inhibitor[22]. This is the case at room temperature where all polymer chains are dormant and retain the nitroxide end-group. On the other hand, if the temperature is too high or if the system is not adequate, K might be too high and poor control over the polymerisation is induced as radical termination reactions become too important[14]. Ideally, the $P_n^{\cdot}$ concentration should be low enough to minimise side reactions in such a way that they become negligible. Suitable conditions for efficient polymerisation are usually met in the temperature range of 90 to 140 °C, depending on the monomer and nitroxide used[1]. Another important factor is that the optimal values for k_d and k_c are directly correlated to k_p and k_t[20]. In order for all the polymer chains to statistically grow at the same time from a macroscopic point of view, it is important that the exchange between dormant and active species is much faster than the propagation and termination steps[23]. Another feature is that chain transfer reactions that can occur in free-radical polymerisation can be expected in NMP: e.g. transfer to the monomer[24, 25] as well as transfer to the nitroxide itself[26, 27]. This will generate P_nX species in which X is a fragment of the transfer agent (Scheme 1). This is especially the case when compounds with very high transfer constants, C_{tr} ($C_{tr} = k_{tr}/k_p$), are present, as the transfer reaction will be favoured over propagation. However, transfer reactions are often regarded as side reactions that will hamper the control over the polymerisation and, in a typical NMP experiment, the formation of P_nX should be minimised as much as possible. For this reason, there was no real interest in literature to investigate the use of transfer agents in NMP.

When all the suitable parameters are met according to the mechanism proposed in Scheme 1, the nitroxide group is attached to the resulting polymer chain after terminating the polymerisation[28]. Since the nitroxide-monomer bond is thermally instable, heating the polymer to temperatures above 70 °C to 100 °C leads to homolytic cleavage yielding the nitroxide and a radical on the polymer chain-end. The polymer is, in fact, a macroinitiator, which can be used to reinitiate the NMP process in the presence of a second monomer, thereby generating block copolymers[29, 30]. However, if an end material is sought, the polymerisation thermodynamics might become unfavourable at high temperature as the importance of entropy rises accordingly[31], which will induce depropagation processes[32, 33]. Furthermore, the generated chain-end radical can engage in side reactions such as backbiting and chain-scission[34]. It is well known that most thermoplastics are usually

processed at temperatures around 200 °C or more[35] where they are in their viscous flow region[36]. This flowing behaviour, together with diffusion, will promote side reactions due to the reactive chain-end radical and might eventually degrade the properties of the final product. From an industrial point of view, this aspect makes NMP less attractive for production on large scale.

To overcome these problems, many strategies were employed in order to remove the terminal nitroxide and improve the thermal stability of the resulting polymer. For example Solomon et al.[37] used zinc-acetic acid reduction to transform TEMPO chain-ends into –OH groups. Malz et al.[38] employed a strategy in which polystyrene (PS) synthesised with TEMPO was reduced with lithium aluminium hydride. They also oxidised the TEMPO end-group by adding *m*-chloroperbenzoic acid (MCPA) at room temperatures or by heating the polymer in the presence of 2,6-di-*tert*-butyl-4-methylphenol (Ionol). A similar procedure was employed by Howell and Chaiwong[39] with 2,6-di-*tert*-butyl-4-methylphenol (BHT) as reductive agent. Petit et al.[40] used a transfer reaction with thiophenol to deactivate PS prepared in the presence of SG1. Nicolas et al.[33] adapted this method to poly(methyl methacrylate) (PMMA) bearing SG1 chain-ends. Wong et al.[41] reported the use of tributyltin hydride as radical quencher for the removal of the alkoxyamine function from polymers prepared by enhanced spin capturing polymerisation. Harth et al.[42] developed a method based on the controlled monoaddition of maleic anhydride and maleimide derivatives to generate functional polymers and remove the 2,2,5-tri-methyl-4-phenyl-3-azahexane-3-nitroxide (TIPNO) end-groups. O'Bryan and Braslau[43] employed cerium ammonium nitrate (CAN) to cleave the N-alkoxyamine bond of PS samples to form secondary benzylic cations at the polymer terminus, which can subsequently be trapped by water, alcohols, or nitriles to form the corresponding alcohol, ether, or amide chain-end functionalised polymers. The same strategy was then later employed to synthesise macrocyclic polymers[44]. More recently, Guillaneuf et al.[45] reported the nearly quantitative radical bromination and subsequent radical azidation of SG1 terminated PS in the presence of ethyl 2-bromoisobutyrate and ethanesulfonyl azide respectively. The brominated polymer was used as ATRP macroinitiator to synthesise a block copolymer.

Although the methods previously mentioned provide a successful way for the removal of nitroxide end-groups while, in some cases, introducing different functional groups, all of them involve post-polymerisation reactions and additional purification steps. This is a major drawback for industrial purposes, where simplicity and short reaction procedures are well appreciated. In a system that possesses some analogy with NMP, Debuigne et al.[46] described the quenching of cobalt-mediated radical polymerisation in one-pot by radical scavengers such as thiols and nitroxide in order to remove the cobalt complex from the polymer chain-ends.

In this paper, a simple one-pot procedure for the nitroxide end-group removal of synthetic polymers prepared by NMP is presented. The approach is based on the controlled addition of dodecanethiol, thiophenol, radical initiators or carbon tetrabromide as terminating agents for the NMP of styrene, isobornyl acrylate and methyl methacrylate. Furthermore, different initiating systems and nitroxides such as TEMPO and SG1 were investigated. The thermal stability of the resulting polymers, as well as their potential application as ATRP macroinitiators, was also looked for.

EXPERIMENTAL PART

Materials. Benzoyl peroxide (BPO), 1-dodecanethiol (≥ 98%), thiophenol (99%), carbon tetrabromide (CBr_4; 99%) and silver trifluoroacetate (AgTFA, 98%) were purchased from Sigma-Aldrich and used as received. 2,2'-azobis(isobutyronitrile) (AIBN) was purchased from Merck and recrystallised twice from methanol before use. 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) was purchased from Sigma-Aldrich and sublimed before use. 3,7-dioxa-4-aza-6-phosphanonanoic acid, 4,5-bis(1,1-dimethylethyl)-6-ethoxy-2,2-dimethyl-, 6-oxide (MAMA-SG1) and N-*tert*-butyl-1-diethylphosphono-2,2-dimethylpropyl nitroxide (SG1) were kindly supplied by Prof. Richard Hoogenboom (UGent). Styrene (S) (99%, extra pure, Acros Organics) was freshly distilled over Ca_2H, and then kept under nitrogen atmosphere in a Schlenk flask. Methyl methacrylate (MMA) was purified by freshly distilling it over Ca_2H prior to use. 1-Ethoxyethyl acrylate (EEA) was prepared following the procedure of Van Camp et al.[47]. Isobornyl acrylate (iBA; Aldrich, tech.) was purified by vacuum distillation (394 K/18 mmHg). Copper(I) bromide (Cu(I)Br; Aldrich, 98% (metal

based)) was purified by stirring with acetic acid, then by filtering and washing with ethanol and diethyl ether, and finally by drying in a vacuum oven at 343 K. *N,N,N',N'',N''*-pentamethyl diethylenetriamine (PMDETA; Acros, 99+ %) was freshly distilled prior to use (358-359 K/12 mmHg), and kept under argon atmosphere. The solid chain transfer agents (BPO, AIBN, and CBr_4) were dissolved in a minimum amount of *o*-xylene, and the resulting solution was degassed under argon prior to use. The other liquid chain transfer agents (1-dodecanethiol and thiophenol) were also degassed under a smooth argon flow prior to use. All solvents employed were purchased from Sigma-Aldrich (HPLC grade), and used without further purification.

Synthesis of polymers by NMP. (A general procedure is described here. More details can be found in the electronic supporting information (ESI) provided). A monomer (M), the corresponding initiating system (bimolecular initiator with AIBN and the corresponding nitroxide or unimolecular initiator with MAMA-SG1) were gently stirred during 30 min, transferred into a Schlenk vessel, and then conveniently degassed by three freeze-pump-thaw cycles. Subsequently, the vessel was backfilled with nitrogen gas, and the reaction mixture was then immersed in an oil bath, which was preheated at the reaction temperature. The polymerisation was conducted under nitrogen atmosphere with magnetic stirring. For kinetic analyses, samples were withdrawn from the reactor. The monomer conversions were determined by ^1H NMR analysis on crude samples dissolved in $CDCl_3$. Molecular weights were determined by size exclusion chromatography (SEC). When the desired molar mass and conversion were obtained, a crude sample from the reaction mixture was cooled, diluted with THF, and precipitated into an excess of methanol. The remaining reaction mixture was reacted with different chain-transfer agents (1-dodecanethiol, thiophenol, AIBN, BPO or CBR_4). Typically, the transfer agent was added to the reaction mixture under a smooth nitrogen flow, and left to react for at least 10 minutes up to 1 hour. After that, the crude reaction mixture was cooled with ice or liquid nitrogen, diluted with THF, and precipitated into an excess of chilled methanol or heptane. The resulting polymers were isolated by filtration and dried under vacuum (10^{-2} mmHg) at 298 K for 2 h to yield a dry powder.

The different samples obtained by the procedures described above were subjected to physicochemical analyses (NMR, SEC, MALDI-TOF MS, TGA). Also, the bromine terminated polymers were employed as macroinitiators during ATRP experiments, which are described as follows.

Chain extension by using bromine terminated macroinitiator and ATRP. (More details can be found in the ESI provided). A typical ATRP experiment was carried out as follows. First, a mixture of a bromine terminated homopolymer (P-Br), the monomer for chain extension, and PMDETA was gently stirred during 30 min. Then, it was transferred to the Schlenk reactor, and degassed by three freeze-pump-thaw cycles. Subsequently, it was backfilled with nitrogen, and Cu(I)Br was added under a smooth nitrogen flow. One aliquot of this mixture was taken, after which the reaction flask was placed in an oil bath set at the reaction temperature. At distinct polymerisation times, samples were withdrawn from the reaction system to determine the conversion and the polymer properties. Finally, 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.

Characterisation

NMR. ^{1}H nuclear magnetic resonance (NMR) spectra were recorded at 300 or 500 MHz in $CDCl_3$ solution at room temperature on a Bruker Avance 300 or Bruker DRX 500 spectrometer, respectively. A relaxation delay of 30s between scans was applied to ensure quantitative results. ^{31}P NMR was measured on a Bruker Avance 300 apparatus fitted with a BBO probe at 121.49 MHz with conditions for quantitative analysis: 64 scans and relaxation delay of 90s between scans. Due to the low amount of SG1 compared to the polystyrene chains, a high of amount of product (200 mg) was dissolved in 0.8 mL of $CDCl_3$. Chemical shifts are presented in parts per million (δ).

SEC. Size Exclusion Chromatography (SEC) analyses were performed on an Agilent (Polymer Laboratories) PL-GPC 50 plus instrument, using a refractive index detector, equipped with two PLgel 5 μm MIXED-D columns thermostated at 40 °C. PS and PMMA standards were used for calibration. PS and PiBA samples were analysed using PS

calibration while PMMA samples were analysed using PMMA calibration. THF was used as eluent at a flow rate of 1 mL/min. Samples were injected using a PL-AS RT autosampler.

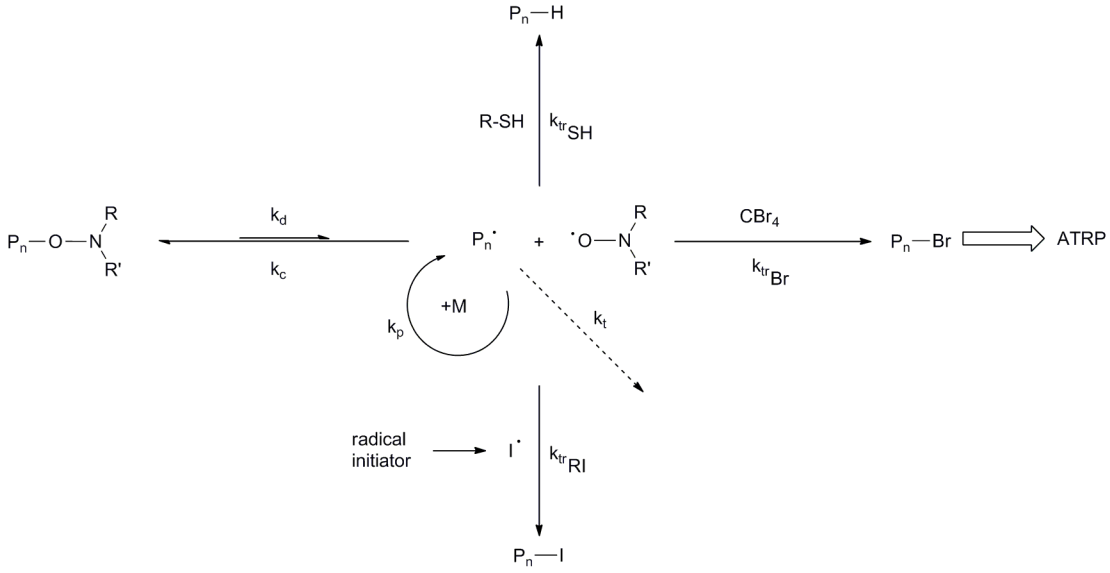
Matrix assisted laser desorption/ionization time of flight mass spectroscopy. MALDI-TOF MS was performed on an Applied Biosystems Voyager De STR MALDI-TOF spectrometer equipped with 2 m linear and 3 m reflector flight tubes, and a 355 nm Blue Lion Biotech Marathon solid state laser (3.5 ns pulse). All mass spectra were obtained with an accelerating potential of 20kV in positive ion mode and in linear and/or reflector mode. Trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene]malonitrile (BMPM) (20 mg/mL in THF) was used as a matrix, AgTFA (1 mg/mL) was used as a cationising agent, and polymer samples were dissolved in THF (2 mg/mL). Analyte solutions were prepared by mixing 10 μL of the matrix, 5 μL of the salt, and 5 μL of the polymer solution. Subsequently, 0.5 μL of this mixture was spotted on the sample plate, and the spots were dried in air at room temperature. A poly(ethylene oxide) standard (PEO, M_n = 2000 g.mol^{-1}) was used for calibration. All data were processed using the Data Explorer 4.0.0.0 (Applied Biosystems) software package.

TGA. Thermogravimetric analysis (TGA) was performed with a Mettler Toledo TGA/SDTA851e instrument under N_2 atmosphere at a heating rate of 10 °C/min between 25 and 800 °C.

RESULTS & DISCUSSION

In order to improve the stability of polymers synthesised by NMP, it is necessary to remove the nitroxide and neutralise the polymer chain-end in an efficient and clean way. As shown in Scheme 2, it is expected that the use of transfer agents with very high transfer constants, C_{tr}, will yield the desired product. To confirm this hypothesis we developed a one-pot two-step process. First, polymerisation by NMP proceeds under standard conditions for the monomer of choice. Secondly, when the desired molecular weight and conversion are reached, the transfer agent is added. After a few minutes, all the propagating polymer chains are terminated and the transferred radical may be able to initiate new

polymer chains. In order to avoid a bimodal molar mass distribution, the reaction is quenched only a few minutes after addition of the corresponding transfer agent, and purification by standard procedures is then performed. Furthermore, if the chosen chain transfer agent is able to provide a functional group, this new methodology opens the way to one-pot functionalisation of polymers produced by NMP.



Scheme 2 One-pot nitroxide removal and direct synthesis of a macroinitiator for ATRP.

Compounds having the highest transfer constant, C_{tr}, in free-radical polymerisation of styrenics, acrylates and methacrylates were chosen as, by analogy, it is expected that those compounds would exhibit the highest activity in NMP. The transfer agents chosen were thiols, radical initiators and carbon tetrabromide. Their uses and efficiencies are described separately in the following paragraphs.

Thiols

In order to study the one-pot nitroxide removal using thiol compounds, different monomer and initiating systems were proposed: PS with TEMPO and SG1 as well as PiBA and PMMA with SG1 (Table 1). As shown in Scheme 2, chain transfer with thiols occurs through hydrogen abstraction from the thiol, which will result in thermally stable hydrogen terminated polymers. From literature it is known that the transfer constants of aliphatic thiols are very high in free radical polymerisation of styrene (C_{tr} = 16 for 1-dodecanethiol at

60 °C in bulk[48]) and acrylates (C_{tr} = 1.5 for butyl acrylate (BA) with 1-dodecanethiol at 60 °C in bulk[49]). Furthermore, in the case of acrylates, thiols are also susceptible to react with mid-chain radicals, thereby limiting the side reactions they can induce[50]. Although smaller, the transfer constant for MMA is also relatively important with aliphatic thiols (C_{tr} = 0.7 for 1-dodecanethiol at 60 °C in bulk[49]). However, higher transfer constants were observed with thiophenol during free radical polymerisation of MMA (C_{tr} = 2.7 for thiophenol at 60 °C in bulk[51]). For this reason we were interested to compare the activity of the different types of thiols. Moreover, 1-dodecanethiol was chosen as aliphatic thiol as it is widely used in industry and has a limited smell when compared to lower molecular weight aliphatic or aromatic thiols.

Table 1 Experiments for one-pot removal of nitroxides from NMP polymers with thiols[a].

Entry	M[b]	Initiation	DP[c]	T (K)	Thiol	Eq.[d]	$t_i - t_f$[e] (min)	$M_{p,i} - M_{p,f}$[f] ($g.mol^{-1}$)	$conv_i - conv_f$[g] (%)
1	S	AIBN / SG1	412	393	1-dodecanethiol	1	180 – 240	40,800 – 43,500	54.0 – 64.0
2	MMA[h]	MAMA-SG1[i]	244	363	1-dodecanethiol	10	120 – 180	20,900 – 21,900	67.3[j] – 70.8[j]
3	MMA[h]	MAMA-SG1[i]	240	363	thiophenol	10	120 – 180	21,200 – 21,200	68.7[j] – 68.2[j]
4	iBA	MAMA-SG1[i]	245	393	thiophenol	10	60 – 120	12,500 – 14,000	29.6 – 38.7
5	S	AIBN / TEMPO	233	408	1-dodecanethiol	1	180 – 210	7,300 – 7,500	14.2 – 16.0

[a] Further details on the polymerisation conditions can be found in the ESI. [b] M = monomer. [c] Theoretical degree of polymerisation at 100% conversion. [d] Thiol equivalents compared to the nitroxide. [e] t_i = thiol injection time; t_f = final reaction time. [f] $M_{p,i}$ = molar mass just before thiol injection; $M_{p,f}$ = molar mass at the end of the reaction. [g] $conv_i$ = conversion just before thiol injection; $conv_f$ = conversion at the end of the reaction. [h] 8.8 mol% of S was added to ensure control over the polymerisation[14]. [i] 10 mol% of SG1 was added to improve control over the polymerisation[14, 52]. [j] Conversion of MMA only, S was not considered.

For styrene, the systems were based on bimolecular initiation (entries 1,5, Table 1), for practical reasons, but it had no influence on the transfer to thiols as those were added well after completion of the initiation step and similar results would be expected with unimolecular initiation. M_p (peak molecular weight) was used to compare if the molar masses of the original chains were still increasing 30 min (entry 5, Table 1) or one hour (entries 1, 2, 3 and 4, Table 1) after thiol addition. This was necessary because the thiol does not stop the propagation but merely transfers the propagating radical, which will in turn generate new polymer chains. Since the transfer agent is still present, it is likely that the reinitiation / NMP / termination cycle continues until the reaction is stopped, thereby producing oligomers, some of which might possess the nitroxide end-group. Hence, the

result is that M_n will be lowered and PDI will increase significantly (see ESI, Table S1). This is visible in

Figure 1, which corresponds to entry 1 in Table 1, and in which the molar mass of the polymer increased regularly with time during the NMP process. However, after 3h, when 1-dodecanethiol was added, the molar mass increase stopped and, 30 min later, a second lower molar mass distribution was observed. On the other hand, M_p was found to increase very little one hour after thiol addition, which indicates that the initial propagating chains are effectively terminated. A noticeable fact is that no oligomer shoulder was observed 10 min after addition of the thiol to the system. Furthermore, similar trends were observed for all monomers and initiating systems (entries 2-5, Table 1), which confirms that the procedure can be regarded as a universal approach (see ESI). Also, the PMMA chains (entries 2,3, Table 1) were synthesised in the presence of 8.8 mol% of styrene to ensure control over the polymerisation[14]. As a consequence, those polymers contain styrene as a last monomer unit[53], which means that the C_{tr} of the thiol with respect to the styrene radical should be considered.

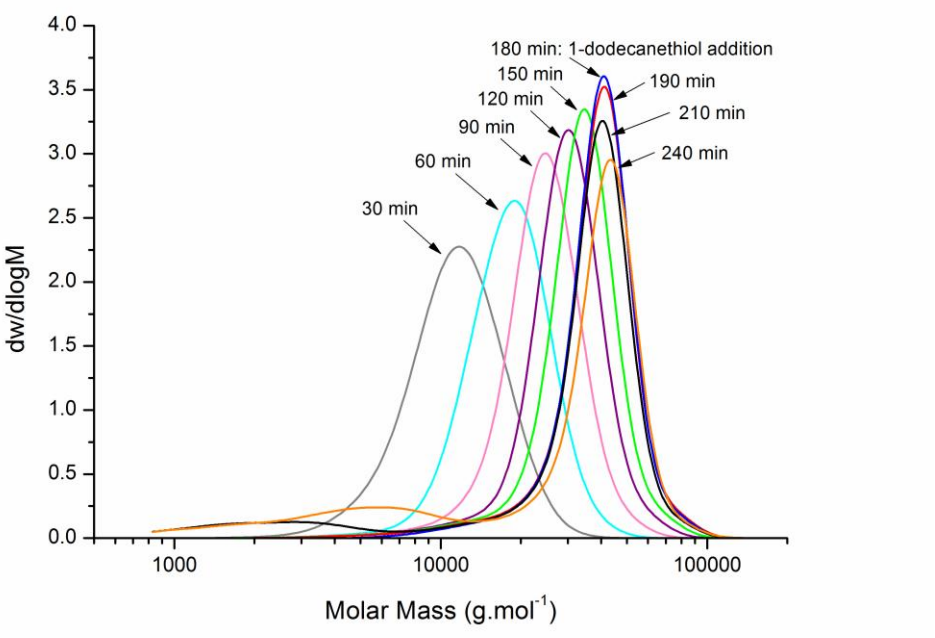


Figure 1 Evolution of molar mass distribution for PS synthesised by NMP and one-pot SG1 removal with 1-dodecanethiol (entry 1, Table 1).

Chain transfer in radical polymerisation can be affected by factors such as chain length and temperature[54]. Therefore the transfer constant value, C_{tr}, for one-pot removal of nitroxides might vary over the whole conversion and degree of polymerisation (DP) ranges. However, the results showed that the propagating chains were effectively terminated for different monomers and at various DP's and conversions (Table 1). This can be explained by the increased C_{tr} at the relatively high temperatures required in NMP, resulting in greater chances for transfer reaction to occur. Similar results were also obtained for the different reactions, both with 1-dodecanethiol and thiophenol (entries 1,5 for styrene and entries 2,3 for MMA, Table 1), which indicates that above a certain C_{tr} value no significant difference was macroscopically observed on the transfer behaviour. Another remarkable feature of the transfer process is that as low as 1 equivalent of thiol compared to the nitroxide is needed (entries 1,5, Table 1), thereby reducing possible smell concerns. This also suggests that other thiols with lower transfer constants might be effective to a certain extent.

Because polymers are usually processed at temperatures well above their T_g's or T_m's[35], their thermal stability is an important parameter for applications. It is known that under these conditions polymers prepared by NMP are prone to earlier degradation due to the presence of the labile nitroxide end-group. However, after transfer reaction with thiols, hydrogen terminated polymers with higher thermal stability are expected. By analysing the samples by TGA before and after thiol addition, this characteristic can be used to confirm the successful removal of the nitroxide in one-pot. In

Figure 2a, TGA results for PS synthesised in the presence of TEMPO (entry 5, Table 1), before and after stabilisation, are shown. When the nitroxide is still present, degradation occurs around 200 °C, which corresponds to the temperature at which polystyrene starts to flow and side-reactions are favoured. However, 1 min after thiol addition the thermal stability of the system is clearly increased. A slight inflection in the curve is still observed around 250 °C but it disappears 10 min after thiol addition. This indicates that most but not all of the nitroxide end-groups were removed after 1 min and that polymer stabilisation was complete 10 min after thiol addition. In Figure 2b, TGA's for PMMA synthesised with SG1 before and after stabilisation are presented. Although the samples seem to contain residual solvent from the purification procedure as shown by the

loss of mass around 100 °C (heptane), the stabilisation effect is also clear since the loss of mass is reduced up to about 400 °C after thiol addition.

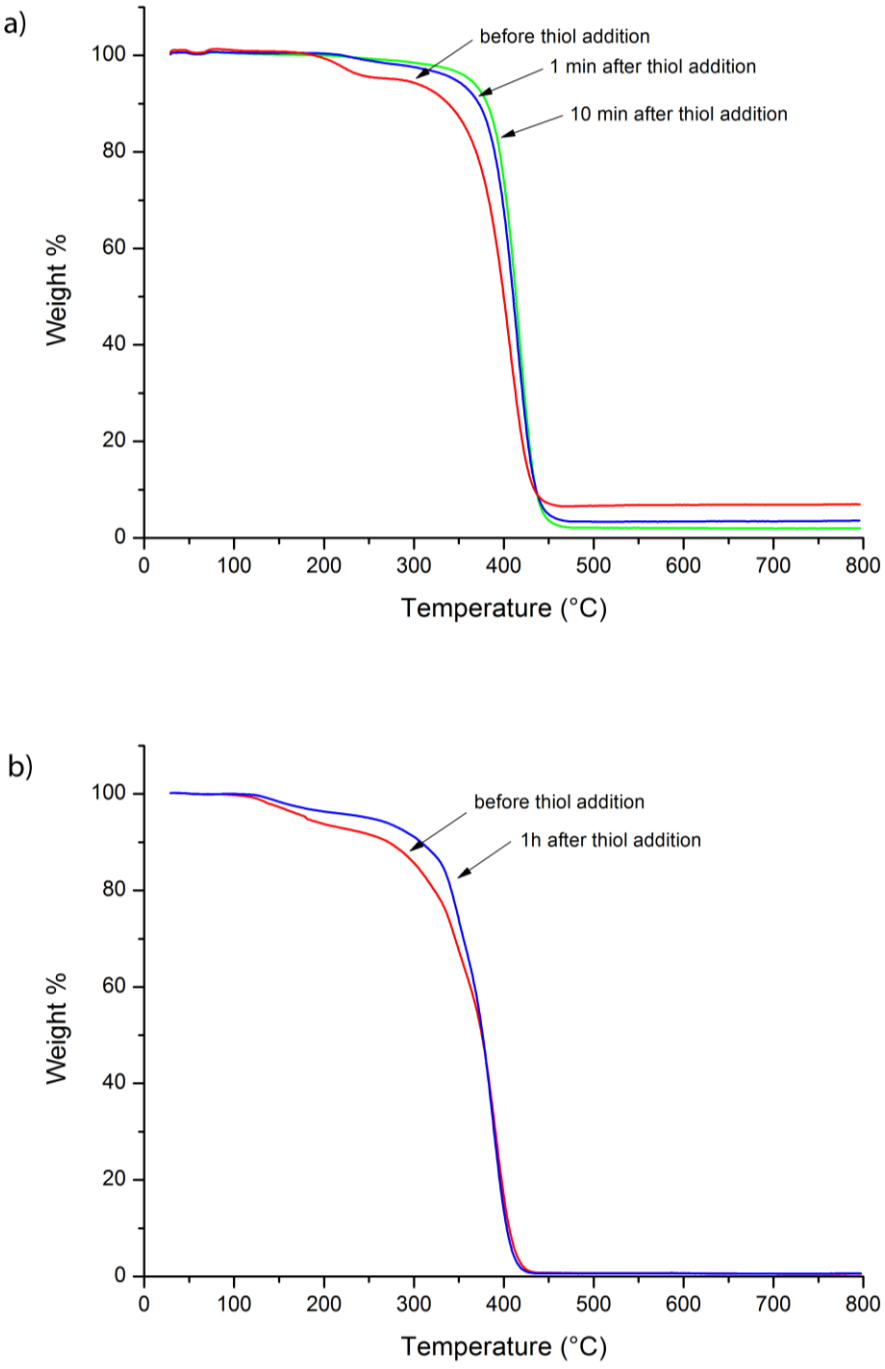


Figure 2 a) TGA before, 1 min and 10 min after 1-dodecanethiol addition for PS synthesised with TEMPO (entry 5, Table 1). **b)** TGA before and 1h after thiophenol addition for PMMA synthesised with SG1 (entry 3, Table 1).

In order to further confirm these results, a MALDI-TOF analysis has been performed on the PS samples (entry 5, Table 1) before and after addition of the thiol compound (Figure 3).

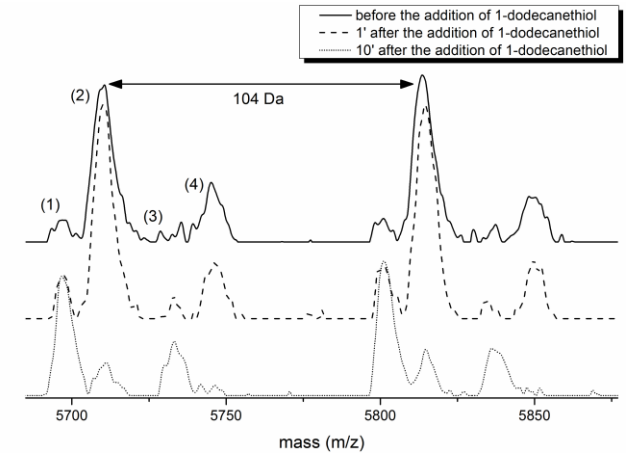


Figure 3 MALDI-TOF spectra of PS synthesised in presence of TEMPO and terminated by 1-dodecanethiol (entry 5, Table 1). Top spectrum: before the addition of 1-dodecanethiol; middle spectrum: 1 min after the addition of 1-dodecanethiol; bottom spectrum: 10 min after the addition of 1-dodecanethiol.

Before the addition of 1-dodecanethiol (Figure 3, top spectrum), up to 3 different series of signals could be observed at a location denoted as (1), (2) and (4). The mass difference between two successive, analogous signals is 104 Da (molar mass of one styrene repeating unit). None of the series corresponds to the theoretical isotope distribution of the expected structure (see ESI, Figures S5-S8) although it is supposed that series (2) and (4) can be attributed to TEMPO terminated PS. This assumption is based on the disappearance of these series upon addition of 1-dodecanethiol (see further). It is known that fragmentation is occurring during MALDI analysis, which gives rise to these series[55]. Series (2) corresponds to the theoretical isotope distribution of AIBN initiated PS and a methylene exo double bond at the end, whereas series (4) can be attributed to a similar structure that was thermally initiated (see ESI, Figure S6). Series (1) is mostly visible at higher molecular weights and corresponds to a small fraction of proton terminated PS (dead polymer chain). One minute after the addition of 1-dodecanethiol, one additional series (3) is appearing while the relative intensity of the other series is changing (Figure 3, middle spectrum). The new series corresponds to proton terminated PS with a thermal initiation group. The decrease of series (2) and (4) in combination with an increase of the proton

terminated series clearly demonstrates the one-pot substitution of the TEMPO end-group from PS synthesised via NMP with a proton. Nevertheless, the reaction does not seem to be completed since the series that could be attributed to the TEMPO terminated PS are still partially visible. After 10 min, series (4) could not be observed anymore and series (2) almost vanished, indicating that the reaction is near to be quantitative (Figure 3, bottom spectrum).

In conclusion, the one-pot removal of nitroxides can be performed as such: the monomer is polymerised under NMP conditions until the desired molar mass and conversion are reached, after which thiol addition occurs and, 10 min later, the reaction is quenched to prevent the formation of oligomers. The stabilised polymer can subsequently be recovered by simple purification methods.

Radical Initiators

The use of thiols as transfer agents does not allow for the replacement of the nitroxide with a different functional group. Thus, other possible alternatives to thiols were investigated. In this respect, another category of compounds active as transfer agents in radical polymerisation, which was extensively studied in literature, are radical initiators. The reason is that transfer reaction to an initiator will affect the polymerisation efficiency and thus the final molar mass and structure of the polymer[56, 57]. However, transfer reactions are depending on the monomer and the initiator system used as well as on the conversion. A perhaps more important feature of radical initiators is their ability, during free radical polymerisation, to react with propagating radicals through primary radical termination events, which can occur by disproportionation or combination[54]. Usually, this phenomenon is small and negligible as the concentration of propagating radicals is higher than that of primary radicals generated from the radical initiator. However, for NMP, the concentration of propagating radicals is much lower than for free radical polymerisation. Thus, it is expected that the controlled addition of a rapidly decomposing radical source will terminate the polymerisation and remove the nitroxide from the growing polymer chains, as shown in Scheme 2. Furthermore, it is presumed that, at the end of the reaction, the nitroxide will be coupled to newly formed oligomer chains or become part of alkoxyamines, which also contain the radical source fragment and one monomer unit[58]. At the temperatures required

for NMP (usually above 100 °C), radical sources such as AIBN and BPO have a half-life of only a few minutes[59]. This is also the reason why these initiators are commonly used for the bimolecular initiation of NMP; in this case it is important that all the chains are initiated at the same time. The experiments performed for the one-pot removal of nitroxide with radical sources are described in Table 2. Styrene polymerisation in the presence of SG1 was used as a model system to investigate their efficiency.

Table 2 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)	$M_{p,i} - M_{p,f}$[e] (g.mol^{-1})	$conv_i - conv_f$[f] (%)
6	446	BPO	10	180 – 240	42,200 – 44,900	51.3 – 96.4
7	476	AIBN	10	180 – 240	39,600 – 41,500	55.5 – 87.4
8	446	AIBN	2	180 – 240	44,200 – 52,700	-
9	443	AIBN	4	180 – 240	49,400 – 54,400	-
10	428	AIBN	10	900 – 1440	87,600 – 84,900	88.2 – 98.9
11[g]	379	AIBN	10	900 – 1440	83,500 – 80,900	-

[a] Monomer: styrene; initiation: AIBN / SG1; temperature: 393 K (Further details on the polymerisation conditions can be found in the ESI). [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] $M_{p,i}$ = molar mass just before radical source injection; $M_{p,f}$ = molar mass at the end of the reaction. [f] $conv_i$ = conversion just before source radical injection; $conv_f$ = conversion at the end of the reaction; - = not determined. [g] 50 vol% of *o*-xylene was also added.

It appears from entries 6 and 7 in Table 2 that the addition of 10 equivalents of BPO or AIBN leads to a dramatic increase in conversion. For example for entry 6, the conversion increased from 51 % before addition up to 96 % after addition. This, however, was expected since monomer was still present when the radical source was added. The sudden concentration increase of initiating radicals could not be counterbalanced by the nitroxide, which was present in lower concentration. The result was that M_n decreased and the PDI increased significantly as the control over the polymerisation was lost (see ESI, Table S2). Nevertheless, the important point is that M_p values are very similar before and after the radical source addition: from 42,200 to 44,900 g.mol^{-1} for entry 6 (Table 2). This indicates that the propagating chains were effectively terminated in a rapid manner. No significant differences were observed between BPO and AIBN. Therefore, only AIBN was chosen for the remaining study.

For entries 6 and 7 (Table 2), the amount of radicals added was so substantial that, while the controlled polymer chains were terminated, oligomers were formed due to the high number of initiation and termination events (Figure 4a).

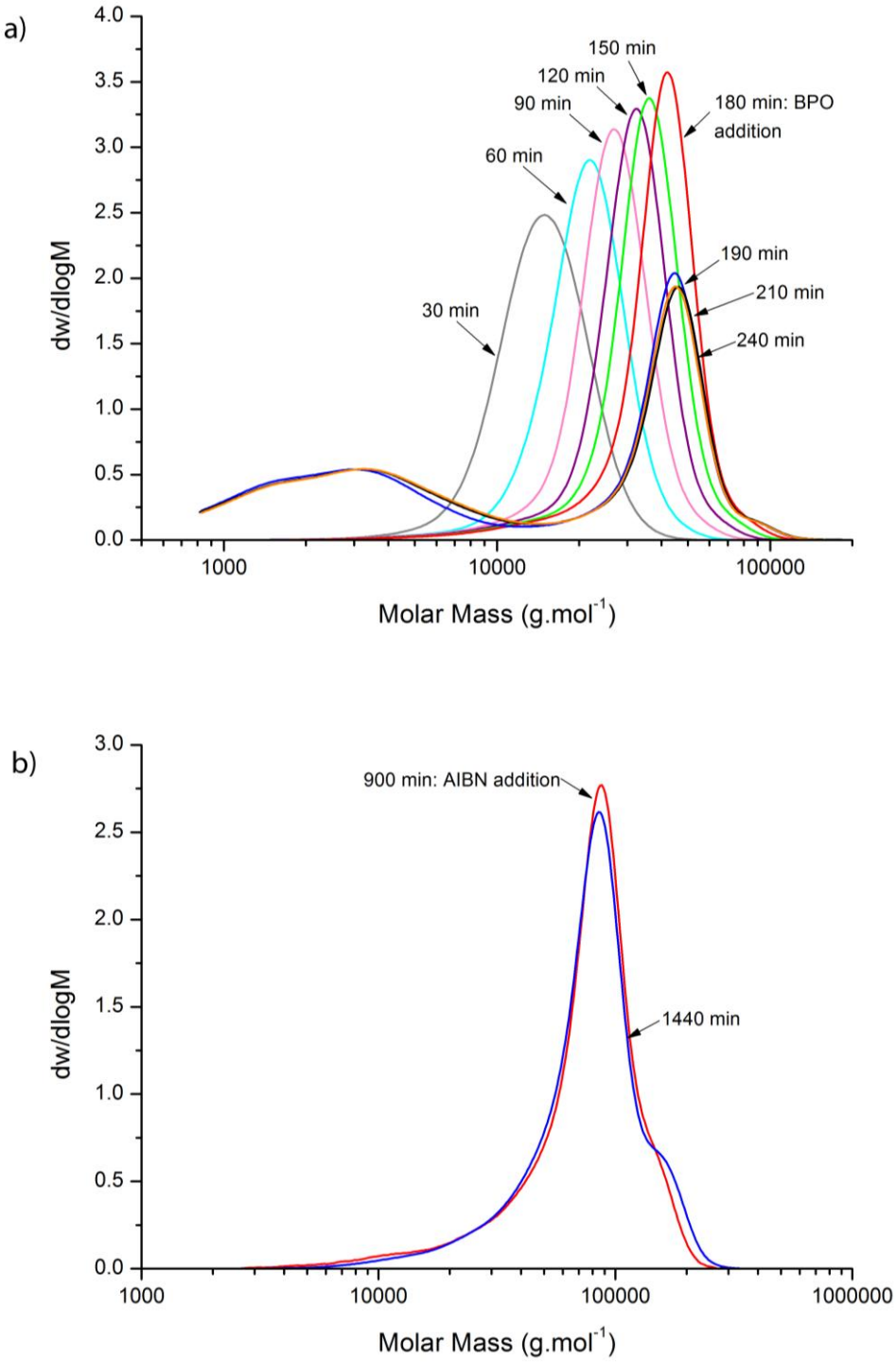


Figure 4 a) Evolution of molar mass distribution for PS synthesised by NMP and one-pot SG1 removal with BPO (entry 6, Table 2). **b)** Evolution of molar mass distribution for PS synthesised by NMP and one-pot SG1 removal at high conversion with AIBN (entry 10, Table 2).

For this reason, the amount of AIBN added was lowered to 2 equivalents (entry 8, Table 2) and 4 equivalents (entry 9, Table 2) compared to SG1. The formation of oligomers was effectively lowered (see ESI, Figures S10 and S11) but M_p values before and after addition increased: from 44,200 to 52,700 g.mol^{-1} for entry 8 (2 equivalents of AIBN compared to SG1) and from 49,400 to 54,400 g.mol^{-1} for entry 9 (4 equivalents of AIBN compared to SG1). This indicates that the growing chains were not terminated immediately and that 10 equivalents of the radical source with respect to the nitroxide are required in order to obtain a fast removal of the nitroxide.

In order to obtain stabilised polymers in a one-pot procedure and avoid the formation of undesirable oligomers, the addition of the radical source was performed at high conversion (entries 10 and 11, Table 2). It can be seen in Figure 4b that there is almost no difference between the SEC traces for entry 10 (Table 2) before and 9h after AIBN addition, at the exception of a small high molar mass shoulder that might result from undetermined side reactions. This is a clear evidence that the lower amount of monomer left in the reaction mixture prevented the formation of oligomers. Also, based on this observation, it is possible to wait more than 10 min between the radical source addition and the end of the reaction. In the case of entry 11 (Table 2), 50 vol% of *o*-xylene was added to the reaction mixture to facilitate the homogenisation of the radical source and displacement of the nitroxide end-groups. However, no significant difference with entry 10 (Table 2) was observed (see ESI, Figure S12).

Halogen: CBr_4

As it is well-described in the literature, controlled radical polymerisation (CRP) techniques have been proven to be a very efficient method for the preparation of functional polymers[60]. In particular, due to the CRP mechanism, polymer chains prepared by such techniques are end-capped by a ‘dormant’ unit, which can be transformed into diverse functional groups after polymerisation. ATRP is probably the most practical technique, because the terminal alkyl halide can be used for standard nucleophilic substitutions or

elimination reactions. Formation of azides, amines, double bonds, sulfide and even thiols have been shown to be feasible by performing an appropriate modification of the ω-halogen end-group of ATRP synthesised polymers[60]. However, depending on the targeted functional group, transformations can be more or less efficient or easy to achieve.

Nevertheless, one of the major disadvantages of ATRP is the use of a transition metal catalyst. For this reason, the preparation of bromine containing polymers via NMP was aimed for. These polymers can be synthesised via a one-pot substitution of the nitroxide end group by a bromine group at the end of a NMP reaction. Such a strategy does not require any transition metal, and furthermore, the experimental procedure is much easier compared to ATRP.

For this purpose, the possibility to use halogens, known as an important class of transfer agents in free radical polymerisation, was investigated. They are known to react by halogen-atom transfer with carbon centred radicals[54]. Halogens usually exhibit lower transfer constants than thiols. For this reason CBr_4 was selected due to the relatively high chain transfer constants with this compound: $C_{tr} = 4.2$ with S at 60 °C[61] and $C_{tr} = 0.15$ with MMA at 60 °C[62]. By a controlled addition of CBr_4 at the end of a NMP reaction, bromine functionalised polymers can be prepared in a one-pot procedure (Scheme 2). This methodology was applied to obtain the corresponding bromine terminated PS-Br, PiBA-Br and PMMA-Br (Table 3), regardless of the initiation system employed (unimolecular or bimolecular, according to NMP theory).

Table 3 Experiments for one-pot removal of nitroxides from NMP polymers with CBr_4[a].

Entry	M[b]	Initiation	DP[c]	T (K)	CBr_4 Eq.[d]	$t_i - t_f$[e] (min)	$M_{p,i} - M_{p,f}$[f] ($g.mol^{-1}$)	$conv_i - conv_f$[g] (%)
12	S	AIBN / SG1	468	393	10	180 – 240	40,800 – 42,800	33.3 – 37.0
13	S	AIBN / SG1	95	393	1	180 – 190	12,600 – 11,000	-
14	S	AIBN / SG1	71	393	1	240 – 250	3,700 – 3,700	-
15	iBA	AIBN / SG1	49	393	1	360 – 370	5,600 – 5,800	-
16	MMA[h]	MAMA-SG1[i]	86	363	1	120 – 130	8,000 – 8,200	-

[a] Further details on the polymerisation conditions can be found in the ESI. [b] M = monomer. [c] Theoretical degree of polymerisation at 100% conversion. [d] CBr_4 equivalents compared to the nitroxide. [e] t_i = CBr_4 injection time; t_f = final reaction time. [f] $M_{p,i}$ = molar mass just before CBr_4 injection; $M_{p,f}$ = molar mass at the end of the reaction. [g] $conv_i$ = conversion just before CBr_4 injection; $conv_f$ = conversion at the end of the reaction; - = not determined. [h] 8.8 mol% of S was added to ensure control over the polymerisation[14]. [i] 10 mol% of SG1 was added to improve control over the polymerisation[14, 52].

For entry 12 (Table 3), a minor conversion increase is observed after CBr_4 addition, with only a 3% increase one hour after the addition. It was postulated that due to steric hindrance, only one Br-group was abstracted from CBr_4, which in turns generate the radical $^{\cdot}CBr_3$. It is expected that this radical can reinitiate the polymerisation to form oligomers. In addition, termination reaction between $^{\cdot}CBr_3$ radicals and propagating radicals on the oligomer chain-ends or another $^{\cdot}CBr_3$ radical is likely to occur[63]. Similarly, the nitroxide can react with either the $^{\cdot}CBr_3$ radical or the propagating oligomer. The advantage in this case is that the reaction can proceed for longer times without the risk of forming an excessive amount of oligomers. This was verified by SEC (

Figure 5) where no low molecular weight shoulder was observed one hour after CBr_4 addition at the exception of a small population below 1000 g.mol^{-1}. Furthermore, the reaction seems to be fast since the M_p values for entry 12 (Table 3) before (40,800 g.mol^{-1}) and after the CBr_4 addition (42,800 g.mol^{-1}) are very similar, which indicates that the propagating chains were terminated almost immediately upon addition.

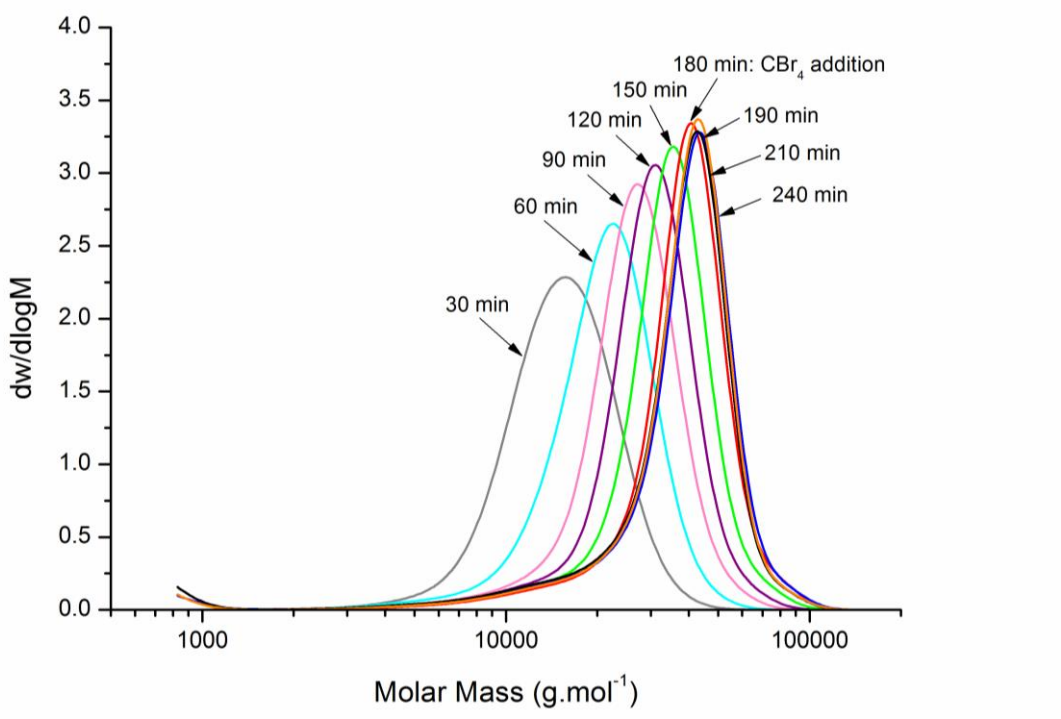


Figure 5 Evolution of molar mass distribution for PS-Br synthesised by NMP with addition of CBr_4 (entry 12, Table 3).

Figure 6 shows the 500 MHz ^{1}H NMR spectrum of a PS-Br (entry 14, Table 3) obtained by applying this methodology. The signal at δ = 4.40 – 4.50 ppm should be undoubtedly attributed to the methine end-group (peak c) directly attached to the bromine atom in PS-Br. According to the spectrum, the intensity of this signal corresponds to the one of a bromine end-group (functionality of 77%). The end-group functionality is not complete, ascribed to the possibility of incomplete bromine substitution and termination in NMP. However, the functionality of 77% found for entry 14 (Table 3), compares well with that determined by Lutz et al. for a PS-Br prepared by ATRP (M_n = 12,000 g.mol^{-1}; conversion = 93.0%; functionality of 76%)[64]. The successful removal of the alkoxyamine moiety was further confirmed by ^{31}P NMR. Figure 7 displays the ^{31}P NMR spectra for entry 14 (Table 3) before (bottom) as well as 1 min (middle) and 10 min (top) after addition of CBr_4. The three measurements were performed with identical concentration. It is clearly noticed that the intensity of the signal at δ = 25 ppm, corresponding to the phosphorus atom in the SG1 nitroxide, has disappeared almost completely 10 min after the addition of the CBr_4 solution, thereby confirming the disappearance of the SG1 end-groups as they are replaced by bromine atoms. Similarly to the thiols, it is necessary to wait at least 10 min or more after the CBr_4 addition to ensure an almost quantitative reaction.

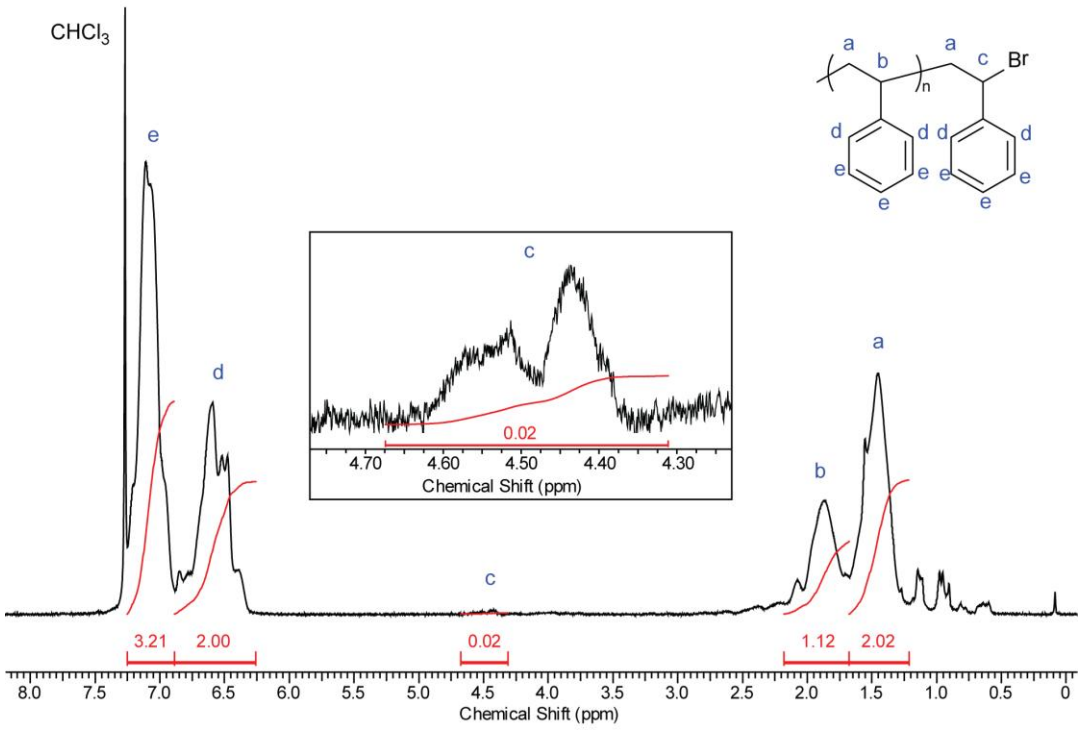


Figure 6 ^{1}H NMR (500 MHz) for PS-Br 10 min after CBr_4 addition (entry 14, Table 3).

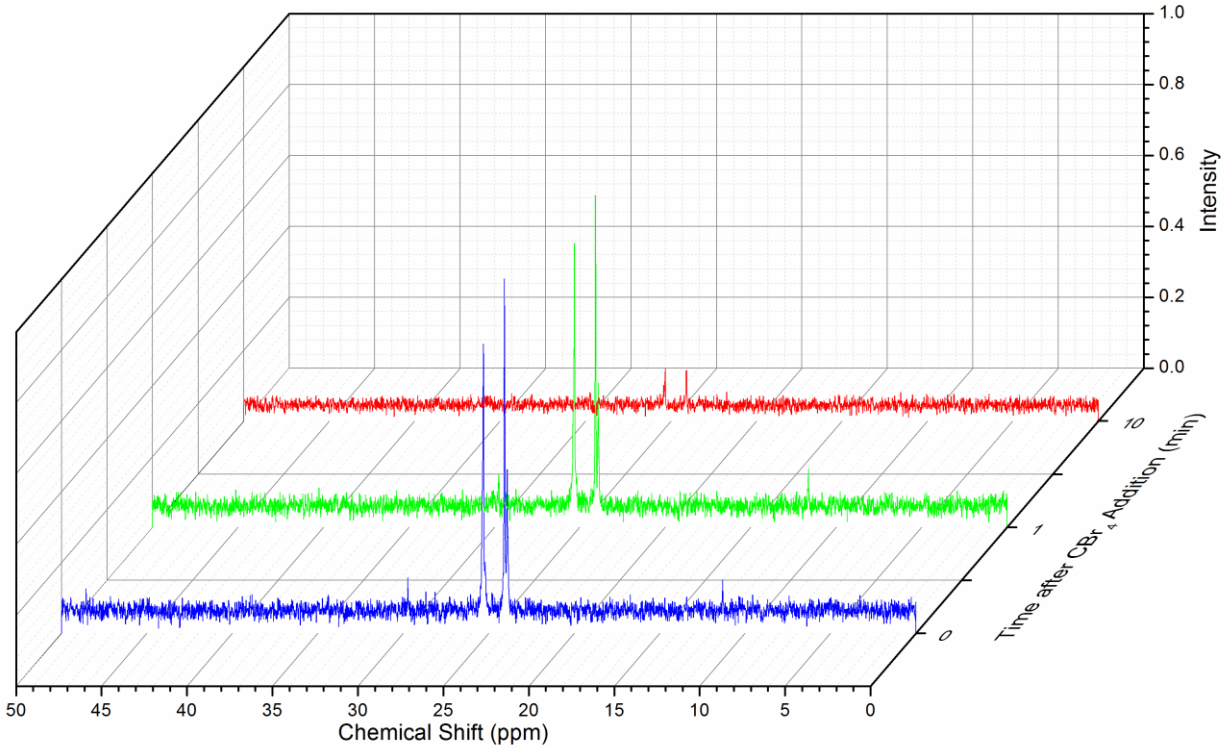


Figure 7 ^{31}P NMR (121.49 MHz) for PS-Br before (bottom) and 1 min (middle) and 10 min after CBr_4 addition (entry 14, Table 3).

In the case of PiBA (entry 15, Table 3), the functionality was determined to be 95% from NMR (see ESI, Figure S18), which is significantly higher than for PS. It is suggested that the transfer reaction to CBr_4 is faster for iBA than S. For PMMA (entry 16, Table 3), the removal of the alkoxyamine moiety by adding CBr_4 was also achieved in a similar manner. Nevertheless, it should be pointed out that the bromine end-group functionality for PMMA could not be determined by NMR due to overlapping signals, but chain extension should provide more insight into the bromine functionalisation of PMMA.

Chain Extension by ATRP

The successful functionalisation of PS, PiBA and PMMA with CBr_4 was also tested by investigating the efficiency of PS-Br, PiBA-Br and PMMA-Br as macroinitiators for ATRP. Chain extension experiments were performed in order to verify the ability of the

bromine terminated polymers to generate higher molar mass polymers. In a typical procedure, a ratio of 300/1/1/1 between monomer, macroinitiator, Cu(I)Br, and PMDETA was employed (Table 4).

Table 4 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]
17	PS-Br (entry 13)	S	300/1/1/1	383	360	10,000	1.07	25,300	1.18
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] Further details on the polymerisation conditions can be found in the ESI. [b] MI = macroinitiator. [c] M = monomer. [d] Molar mass and PDI of the macroinitiator. [e] Molar mass and PDI after chain extension.

Figure 8 shows the SEC chromatographs for the chain extension experiments performed by using styrene as monomer and PS-Br as macroinitiator (entry 17, Table 4). A noticeable shift can be observed by comparing the initial and the final product after 6 h of reaction. This shift is a clear evidence for the presence of the bromine end-group in the macroinitiator, which proves the suitability of the functionalisation procedure. Nevertheless, it should be pointed out that a shoulder can be seen at low molar masses, which should be considered as a low fraction of non-functionalised PS-Br or unexpected termination reactions. In addition a small amount of coupling can be observed, but with limited importance by judging the PDI evolution before and after functionalisation: from 1.07 to 1.18 for entry 17 (Table 4) and 1.06 to 1.31 for entry 18 (Table 4).

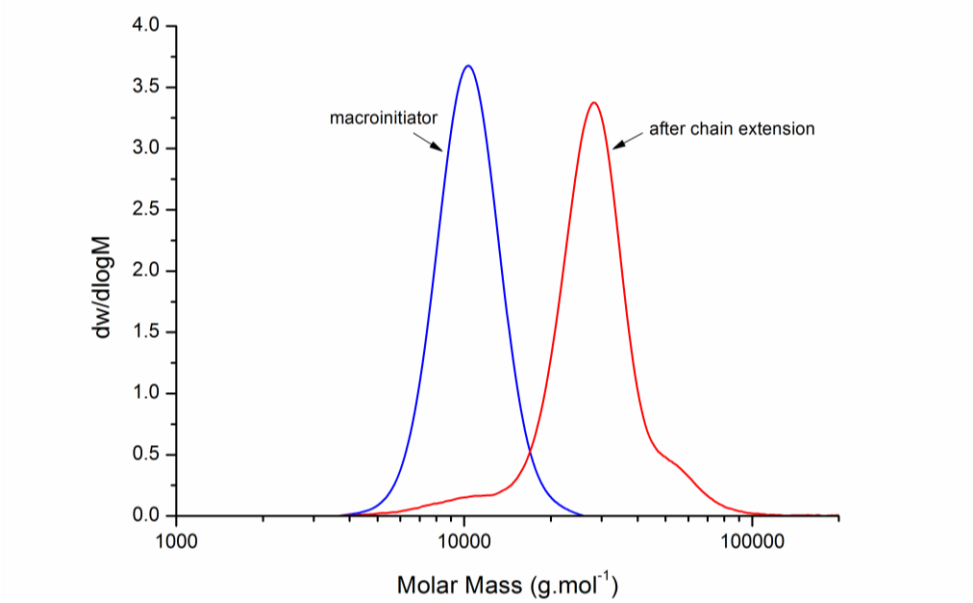


Figure 8 Molar mass distribution before (left) and after (right) chain extension of a PS-Br macroinitiator by ATRP (entry 17, Table 4).

Similar experiments were performed by using PiBA-Br (entry 19, Table 4) and PMMA-Br (entries 20 and 21, Table 4) as macroinitiators with, respectively, iBA and MMA as the chain extension monomers. For PiBA-Br the chain extension occurred as expected although the molar mass increase was small: from 5,200 to 7,000 $g.mol^{-1}$ after 21h of reaction. It is believed that the bulkiness of the growing PiBA$^{\cdot}$ radical restricts the access to the monomer, which slows down the polymerisation kinetics. Nevertheless, the molar mass increase suggests that the bromine functionalisation of PiBA (entry 15, Table 3) was successful. For PMMA chain extension (entry 21, Table 4), a noticeable molar mass increase occurred after 4h of reaction, which is again a clear evidence for the successful chain extension due to the presence of the bromine end-group in the PMMA macroinitiator. Nevertheless, the end product possesses a high PDI (above 2) ascribed to a shoulder at low molar masses[65] (see ESI, Figure S23). Another experiment performed by using a higher catalyst to ligand ratio (1 instead of 0.5) showed a similar trend (entry 20, Table 4). These facts may account for a low fraction of unfunctionalised macroinitiator present in PMMA-Br as a result of termination events during the synthesis of the precursor, or the presence of PMMA-S-Br due to the use of a low amount of styrene during the NMP of MMA[14, 53], which would not exhibit a sufficient dissociation rate constant to ensure a proper initiation

of MMA by ATRP. Additional kinetic experiments would be needed in order to further elucidate this mechanism, but such studies are out of the scope of this paper.

CONCLUSION

A novel and straightforward method based on transfer reactions with highly active compounds allowed for the one-pot stabilisation and functionalisation of polymers prepared by NMP. The controlled addition of transfer agents such as thiols, radical sources and CBr_4 during NMP replaced the labile nitroxide end-group with respectively a hydrogen, a radical initiator fragment or a bromine through a chain transfer reaction in an almost quantitative manner. Furthermore, the universality of the strategy was demonstrated with different monomers such as styrene (S), isobornyl acrylate (iBA) or methyl methacrylate (MMA) as well as various initiating systems and nitroxides (TEMPO and SG1).

1-dodecanethiol and thiophenol performed very well as transfer agents for all monomers studied, as well as for wide molar mass and conversion ranges. Their use clearly improved the thermal stability of the final products. The use of radical sources showed to be appropriate for the removal of the nitroxide end group only in the case where high conversion is attained for the NMP reaction. This was necessary in order to prevent the formation of oligomers. It is also envisioned that the use of functional initiators could provide functional polymers.

CBr_4 was successfully used to synthesise bromine terminated polymers in a one-pot approach. Chain extension experiments by ATRP proved the high degree of functionalisation of the macroinitiators. This switch from NMP to ATRP could provide a simple route towards block copolymers that could not be synthesised exclusively by one of these methods.

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